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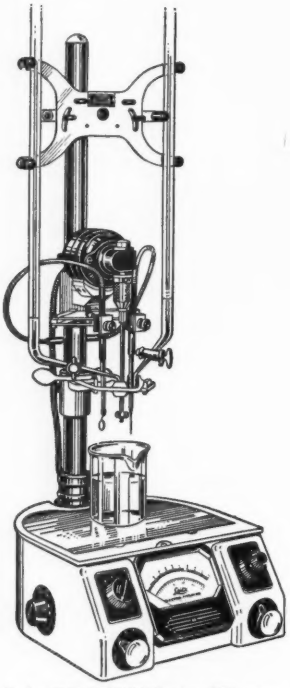

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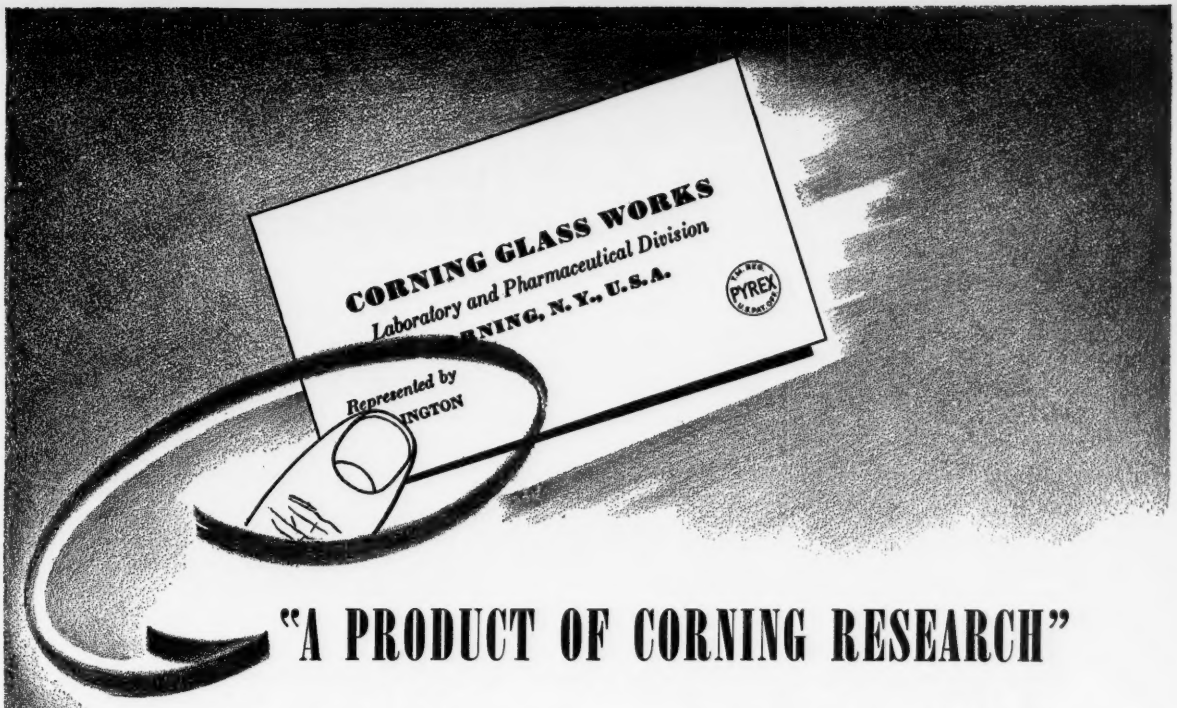

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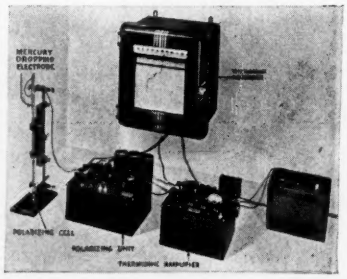

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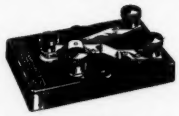

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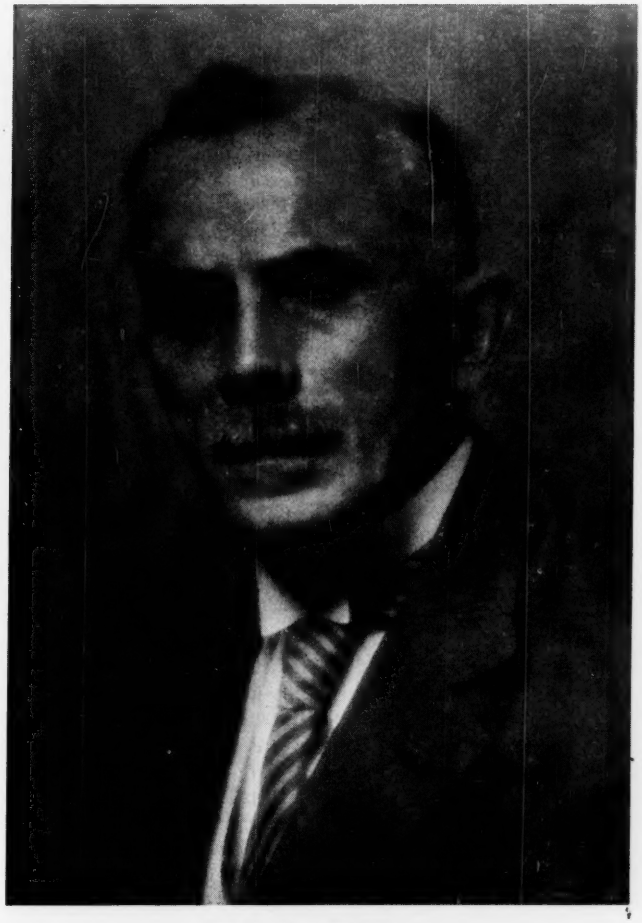

Wilhelm Böttger
(1871–)

Contributed by Ralph E. Oesper, University of Cincinnati

(For biographical sketch of Wilhelm Böttger, see page 24.)

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Editor's Outlook

THE quotation from Ipatieff, on page 46 of this issue, brings up a question which has been on our mind for a long time. His suggestion that we scrap a large portion of the conventional content of organic chemistry is more than a negative one. And it is by no means limited to the organic field. Teachers of elementary and general chemistry have been at least dimly aware of the same situation for a long time. When you continue to pump gas into a container already loaded with a multitude of partial pressures the total will eventually reach the bursting point. This JOURNAL has long advocated the modernization of our elementary courses and textbooks, and will continue to do so; but we sometimes lose sight of the fact that progress involves not only the adoption of new ideas but the elimination of the old.

The human mind, to be sure, seems to be indefinitely elastic; it is not necessary to forget an old fact every time a new one is learned. But our textbooks are made of more resistant material, and if we are not to make it impossible for our students to carry the knowledge around (either in their arms or in their heads) we must soon begin melting up some type. New developments, which appear with constant acceleration, are often fundamental, and their adoption compels the discard of older views no longer tenable. Although there may be a little delay in this "cleaning up" process—as we believe is the case right now in some fields we could mention—this is not the greatest difficulty. It is far easier to distinguish what is fundamentally wrong than that which is relatively useless.

We all know that the chemistry of today is vastly different from that of twenty years ago, not only in its content but in many of its fundamental points of view. But the mental inflexibility of those of us who learned our chemistry two or three decades ago too often keeps us from recognizing the situation. There are plenty of examples of actual errors of fact which have been perpetuated in our textbooks simply because they have become traditional. Furthermore, we are probably over impressed by the argument for an historical approach. Perhaps we have a feeling that this is the method of science, but whether or not that is the case it can be a real hindrance in the teaching of chemistry. The recapitulation of the phylogeny of the race may be the method of biological evolution, but that pattern should not require each student to repeat all the mental wanderings of the generations of his predecessors. This is a streamlined age, in which points are sharpened, curves are flattened, supports are built internally, and we no longer put sockets for buggy whips on turret-top sedans.

So let us give serious attention to the things we can *eliminate* from our courses: facts which are no longer significant, or upon which nothing longer depends; processes which have lost their practical importance; theoretical views which do not contribute to the comprehensive picture we are drawing. It is a matter which cannot be left to the judgment of any one of us, for each has his individual bias and prejudice.

Perhaps it would be a good idea to entertain "Nominations for Oblivion." And we will start the list with one of our own: The Law of Multiple Proportions. This has always impressed us as a needless and fatiguing bit of numerical calisthenics. It is entirely absorbed in any comprehensive generalization on combining weights, and even its historical significance is slight, since it seems to have followed, rather than preceded, the formulation of the atomic theory. Any other nominations?

OUT of the discussions of chemistry in relation to national defense comes the interesting observation that chemistry is the largest contributor to the "totalitarian" hopes of nations—at least that angle of totalitarianism which attempts to render a nation self-sufficient and independent of outside sources of supply. In our own case, the list of "strategic materials," obtainable only from abroad, has been cut, by the development of the chemical industry, to one-third of the list in 1920, until it is now reported that we are dependent upon outside sources for only four major materials: tin, rubber, nitrogen, and crude drugs. And it appears that with the exception of the first of these we should soon be able to take care of ourselves. Outside of wartime necessities the principal economic needs of a community are organic, and a fully developed chemical industry should be able to supply such needs out of raw materials almost everywhere present. Note the frequency with which modern materials are advertised as "made from coal, air, and water." Here are the vital elements, carbon, oxygen, nitrogen, and hydrogen. And even the coal may not always be essential, if and when we reach the time when we can utilize the carbon dioxide of the air. There remains, of course, the energy problem. Most of our organic matter eventually gets back into the water and the atmosphere. We must have energy to reverse the process; if not from coal, then what? Oh, well, leave *some* problems for the next generation!

Bergman, Klaproth, Vauquelin, Wollaston[1]

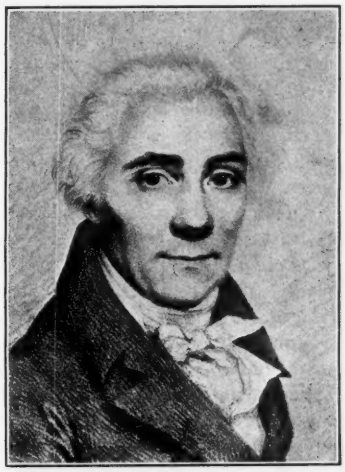
ELSIE GRUEBER FERGUSON Newcomb College, New Orleans, Louisiana

KLAPROTH'S services to analytical chemistry and mineralogy in Germany were performed nearly equally well in France by Vauquelin, twenty years Klaproth's junior. Vauquelin was greatly indebted to Klaproth, his model, but among his countrymen he had no equal in analytical skill. After the death of Lavoisier, Vauquelin, Fourcroy, Guyton de Morveau, and Berthollet were the chief representatives of French chemistry. Said one Frenchman about the relative importance of the first three mentioned: "Lavoisier was creator, Fourcroy apostle, Vauquelin disciple."[2]

Louis Nicolas Vauquelin was born May 16, 1763, in St. André-d'Hébertot, a Normandy village, the son of a farmer on the estate of a Madame d'Aguesseau. When not in the village school, the boy assisted his father on the farm. He readily mastered the subjects taught at the school and also distinguished himself as a student of religion, taught him by the village curé, who became very fond of Vauquelin and who urged him at the age of fourteen to follow his inclination and apprentice himself to an apothecary. He started at Rouen but after a few months there went to Paris, where he was under the protection and friendship of Madame d'Aguesseau and the priests of the order to which the curé of d'Hébertot belonged. For three years he found work in various pharmacies, finally in that of Cheradame, a cousin of Fourcroy. It was there that the latter became interested in him. Shortly after their first meeting Fourcroy, to Vauquelin's great joy, asked the latter to come to his laboratory to work and live with him. Vauquelin soon won the respect and love of Fourcroy as well as of his two sisters, who treated Vauquelin with the greatest kindness. His life here was a very happy one.

Not only was Vauquelin an unusually apt apprentice, but at the same time he continued his studies, really not begun until he went to Rouen, since the schooling at d'Hébertot was of a decidedly inferior rank. He made excellent progress in Latin, Greek, botany, chemistry, physics, natural history, and philosophy. Fourcroy, now his best friend and adviser, insisted on his presenting himself for a master of arts degree at the Athenaeum, a decidedly painful prospect for the very timid Vauquelin, who always spoke hesitatingly and occasionally stammered. However, he passed the ordeal and soon succeeded Fourcroy in teaching the course in chemistry at the Athenaeum. At about the same time, Vauquelin, now about thirty, became a licensed pharmacist and directed a laboratory in the Rue St. Anne.

In 1793, as a result of events following the revolution, Vauquelin was forced to leave Paris. He went to Melun as pharmacist, but fortunately his exile was of short duration. In 1794, probably through the influence of Fourcroy, he was back in Paris as Assistant Professor of Chemistry under Fourcroy and Guyton de Morveau at "L'École Centrale de Travaux Publics," a year later renamed "L'École Polytechnique."



From Weeks's "Discovery of the Elements"
LOUIS NICOLAS VAUQUELIN, 1763–1829

1795 saw him Inspector of Mines. He was asked to give a course in the school of mines in "docimasie," the art of testing the purity of a metal. For the first time he was not living with friends but in the spacious apartment furnished him at the school of mines. On Fourcroy's death in 1811, Vauquelin gave up the greater part of this apartment to Fourcroy's two sisters, who lived there until he died.

After the death of Robespierre on July 20, 1794, Vauquelin was also made a member of the National Institute, now called the Academy of Science. In 1801 he was made Professor of Chemisty in the College of France. Shortly after this Brongniart, member of the Institute and Professor of Chemistry applied to arts at the Jardin des Plantes, died, and Vauquelin became his successor. His selection for this post was distinguished by the remarkable fact that he was unanimously nominated for the position by the Institute, the administration, and the inspector of studies. His lectures covering this three-year course were exceedingly valuable, for he had gathered together information from his years of intensive study and research. Unfortunately, they were not published. Berzelius remarks in his autobiography that listening to lectures of Vauquelin, Biot, and Gay-Lussac convinced him that

[1] Delivered before a seminar in the History of Chemistry at Tulane University, New Orleans, Louisiana, April 27, 1939. Continued from the December, 1940, issue.

[2] BUGGE, "Das Buch der Grossen chemiker," Verlag Chemie, Berlin, **1929**, Vol. I, p. 356.

lecturing was an art which required special study, as well as a natural gift for clearness and ease of expression. Vauquelin had undoubtedly made a special study of it, for although he lacked a natural ease of expression, his students were always most enthusiastic about his lectures.

At the same time that he was lecturing at the Jardin des Plantes, serving as Inspector of Mines, and making for the use of chemists the most difficultly obtainable substances, like phosphorus, he was also Director of the School of Pharmacy. When the Legion of Honor was founded in 1802, Napoleon made him a member.

In 1811 Fourcroy suffered an attack of apoplexy, leaving the Chair of Chemistry at the School of Medicine vacant. Several applied for the position but all others withdrew their applications when they realized that Vauquelin was also seeking it. Soon after this Vauquelin received his doctor's degree, his thesis being a comparison of the composition of human and animal brains. Vauquelin taught at the School of Medicine for eleven years. Then, in 1822, the spirit of reaction after the revolution was responsible for the fact that he and nine others lost their positions. Vauquelin was fifty-nine years old at this time. According to Kopp he was pensioned when he lost his position. He continued working at his other interests, however, and received many honors, including membership in several foreign organizations. Finally in 1828 his home area elected him a deputy, in which position he distinguished himself not by his oratory, but by his diligence, his fine spirit, his determination to make progress without disorder or anarchy, and his devotion to the interests of his country. These same personal traits had characterized all of his dealings and activities. From 1822 on Vauquelin suffered from a "grave malady" which afflicted him for seven years. He died at his birthplace October 1, 1829, at the age of sixty-three.

Vauquelin's career was an unusually successful and fruitful one. His reputation rests on the research he published either alone or with Fourcroy, Humboldt, Klaproth, Chevreul, and Thomson, on his public works, and on his career as educator. Unfortunately there is no collection of his works. They appear mainly in *Annales de Chimie* which, for a time, he edited, and in other French journals, in the *Journal de Physique*, in "l'Encyclopedia Methodique." Vauquelin was interested in many organic substances, including such organic acids as pyromucic and tartaric, and their occurrence in plants. These researches were usually carried out with Fourcroy. It is in inorganic chemistry that his most important contributions were made, however. Kopp, in his discussion of Vauquelin, deplores the fact that although Vauquelin was always alert for new methods of inorganic analysis, he was not as keen at developing or using new analytical methods, nor as able to produce results of the same degree of accuracy, as Klaproth. Many of the mineral analyses of Vauquelin were made on samples that Haüy, who was at the school of mines, gave him. Perhaps the poor analyses made by Vauquelin were not so much due to a lack of precision or technic as to impurities in the reagents and poor specimens presented him by Haüy for analysis. That Vauquelin was, however, an analyst of unusual skill, is seen from the records of his achievements, from which the following selection contains only a small fraction of his contributions.

In 1797 while analyzing a Siberian ore of lead he discovered chromium and described its most important properties and those of its compounds. A year later he isolated this element. The protoxide of chromium was immediately used in painting green on china, and lead chromate was used to dye cotton and calico. In 1798 he discovered in Siberian beryl the oxide of beryllium or "glucinum." This element was isolated by Wöhler and Bussy in 1828. In 1803 he studied platinum, his experiments leading to the discovery of iridium and osmium a year later. In 1813–14 he worked out a method for the separation of lead, palladium, rhodium, iridium, and osmium.

With Fourcroy he found that bones contain magnesium phosphate, fish brains contain phosphorus. He also published papers on alum, on the efflorescence of salts, on tungstic acid, on the ignition of phosphorus in hydrochloric acid, on the combustion of hydrogen in closed vessels, on the respiration of insects and worms, on the volumetric and gravimetric composition of water, on the coloring matter in animal bloods, on the decrease in solubility of one salt due to the presence of another, on dimorphism, and on many other topics. Vauquelin was one of the most versatile chemists. With Fourcroy he proposed one of the most unique varieties of affinity, an "affinité disposante." This exists, they believed, when a substance "acts chemically by means of affinity towards a compound which is not yet formed, but present in the mixture only in the form of its widely separated constituents."[3] For many years chemists in general accepted the existence of a "predisposing affinity."

As Fourcroy had befriended Vauquelin, the latter in turn helped Thenard when he came to Paris. Among his students, who always had the greatest respect and devotion for Vauquelin, can be mentioned: Chevreul, Orfila, Humboldt, Leopold Gmelin, and Stromeyer, a great contributor to mineral analysis. Although he was always shy under normal conditions, he was courageous and bold when occasion demanded. Twice, at the risk of his own life, he rescued unfortunate victims of revolutionary activities. He saved the life of a Swiss soldier who escaped the massacre at the Tuileries but fell into the hands of an infuriated populace. On another occasion, Vauquelin, garbed in the official costume of a member of the Institute, rescued his student Orfila who, along with other Spaniards, had been thrown into prison by Bonaparte. Vauquelin calmly, politely, and successfully merely demanded his release.

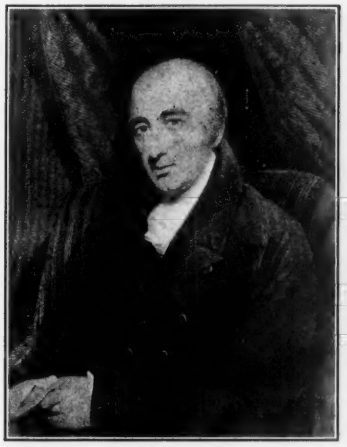
Vauquelin thus rose from his very humble beginning to the enviable position of being the greatest analyst in

[3] KOPP, "Geschichte der Chemie," Friedrich Vieweg und Sohn. Braunschweig. 1843, Vol. II p. 306.

his country, and one of the greatest in Europe. He was fortunate in that he could claim as friends both the curé d'Hébertot, who first encouraged him, and Fourcroy, without whose help the rise of Vauquelin would no doubt have been considerably slower. He was gifted with a fine appreciation and a mind which delighted in the classics, history, and music as well as in science, and with a personality which won for him universal respect and esteem.

It seems difficult to doubt that there is a destiny which guides our paths when we find ourselves discussing in the same classification as ranking chemists of their day men of such diverse backgrounds as Vauquelin and Wollaston. The Dictionary of National Biography lists four Wollastons, beginning with the great-great-grandfather of our William Hyde Wollaston. Into a family which over a period of at least two hundred years had numbered among its members men of the church, poets, members of the House of Commons, philosophers, lawyers, writers, professors, and scientists was born in Norfolkshire on August 6, 1766, England's first great analytical chemist, the third son of an Episcopal clergyman. Unlike most clergymen, Wollaston's father had inherited a great deal of money which, also, had been in the family for generations. Like many of his forebears, William Hyde was sent to Cambridge. He was especially proficient in languages, lecturing as senior fellow in Greek and Hebrew. Through his friendship with John Brinkley, the Astronomer Royal of Ireland, he became interested in astronomy. In 1788 he took a degree in medicine, beginning to practice it in 1789 in Huntingdon and then in Bury St. Edmonds. Here he formed one of the closest friendships of his life—that with the Reverend Henry Hasted. In 1793 he took an M.D. degree from Cambridge. The next year he was made a Fellow of the Royal Society, his certificate having been signed by William Heberden the elder, the most eminent physician of eighteenth century England (who was also, incidentally, Wollaston's uncle), the Honorable Henry Cavendish, Sir William Herschel, and others. In 1797 he set up practice in London, living at 18 Cecil Street on the Thames. No sooner had he built up a very successful practice in London than he abruptly ended his career as a physician by retiring—at the age of thirty-four. The reason for this unexpected decision may have been the fact that another, less able than he, was granted the position in St. George's Hospital for which he had applied, but it may also have been the fact that he was oversensitive and overanxious over his patients, as seen from a letter written to his friend Hasted on December 29, 1800: "Allow me to decline the mental flagellations called anxiety, compared with which the loss of thousands of pounds is as a fleabite."[4]

Wollaston's problem now was to find an income to replace the thousands he had given up, for although his father was monied, the fact that he had fourteen grown sons and daughters besides William Hyde made the share of each a relatively modest one. He therefore decided that he would swell his income through chemistry, bought a home at 14 Buckingham Street, built a laboratory in the rear of the house and before long realized returns on inventions of various kinds. His interests were more varied than anyone else's at the same time except those of Cavendish. The most important of these interests—from a financial standpoint for him and an analytical standpoint for us—was the development, about 1805, of a process for working spongy platinum into a malleable, useful form. This process he kept a secret until shortly before his death when he sold it for 30,000 pounds.



From Weeks's "Discovery of the Elements"

WILLIAM HYDE WOLLASTON, 1766–1828

As early as 1800 began the failure of his eyesight, so unusually fine that with his steady hand he could write with a diamond on glass in handwriting so small that the ordinary eye required a microscope to read the beautifully formed letters. Partial blindness in both eyes resulted. In 1827 his left arm became numb, in 1828 his left pupil became insensitive. When he was told that his symptoms probably indicated a tumor on the brain, he immediately began to dictate papers on his unpublished work. From his bed he directed experiments in progress in the adjoining laboratory until his death on December 22, 1828, at 1 Dorset Street, at the age of sixty-two.

This manuscript prepared just before his death has been lost. However, the other fifty-six papers Wollaston had published are a record of fine achievement in pathology, physiology, chemistry, optics, mineralogy, crystallography, astronomy, electricity, mechanics, and botany. He laid the foundation for the Pulfrich and Abbé refractometers, first drew attention to what is known as Fraunhofer lines (he thought they separated the four colors of the spectrum), invented the reflecting

[4] "Dictionary of national biography," Oxford University Press, London, 1921, Vol. XXI, p. 783.

goniometer which made possible the exact measurement of crystals, immediately used by mineralogists, carried out experiments that finally led to Davy's safety lamp for miners, showed galvanic and frictional electricity to be the same, studied chemical effects of light, wrote papers on methods of comparing light from the sun with that from fixed stars, on calculi of the bladder, on the finite extension of the atmosphere, and on the nature of the triple phosphates. Wollaston's suggestion to the House of Commons in 1814 regarding a standard gallon led to the imperial gallon of the Weights and Measures Act of 1824; he also served on the Royal Commission on Weights and Measures which rejected the decimal system, and with Young as commissioner of the Royal Society on the board of longitude.

These illustrations indicate amply the phenomenal fertility of Wollaston's active mind. Analytical chemistry is indebted to him particularly for the development of a useful form of platinum without which the composition of most minerals would still remain unknown. Wollaston was by no means the first to work on platinum. In 1784 Achard fused arsenic and platinum, got a malleable residue; in 1787 Jeanetty made platinum crucibles, but their cost prevented a general use. In 1800 Richard Knight published a method for preparing malleable platinum by igniting the double chloride of ammonia and platinum. A method similar to this was used by a London firm (Messrs. Johnson, Matthey and Co.), who for many years furnished platinum vessels to laboratories and industries all over the world. It was their method which Wollaston elaborated and his modification which was used for about fifty years. Gentle heating of the chlorides was followed by a manual rubbing of the platinum until it became exceedingly fine. It was pressed while cold in a brass barrel, then compressed with levers. Next it was placed on a charcoal fire and heated to redness to drive off moisture. Finally it was heated at the highest obtainable temperature in a wind furnace for twenty minutes. Then it was placed upright on an anvil, and struck while hot with a heavy hammer. By this method the first platinum vessel for concentrating sulfuric acid, weighing 423 ounces, was made in London in 1809.

Wollaston's work on platinum resulted in his discovery of palladium in platinum ores in 1803. Since he was unwilling to have it known at this time that he was working in platinum, the discovery of palladium was announced in an unusual fashion. He sent to a Mrs. Forster who had a shop in Soho an anonymous note with some palladium asking her to sell this palladium. There was in London at that time an Irishman named Chenevix. During the reign of terror he had been in Paris and was imprisoned there by chance with some chemists who aroused in him an active interest in this science. On his release from prison he distinguished himself as an analyst in a very short time, yet made many enemies because of his crude manner of opposing current philosophical ideas. The unusual method of announcing this element palladium caused him to suspect a fraud which he aimed to uncover. He bought some of this element, studied its properties, and then bought out all of Mrs. Forster's supply. Soon he read a paper before the Royal Society in which he stated that palladium was not, as had been "shamefully announced," a new simple metal but that it was an alloy of platinum and mercury. Wollaston was Secretary of the Royal Society at the time and had made sincere efforts to prevent Chenevix from reading this paper, which was also published in the *Philosophical Transactions*. Wollaston sent another anonymous note, offering a reward of twenty pounds to anyone who would produce a metal like palladium. Interest in this element ran high. Chenevix had prepared an alloy which he found to have the properties the unknown discoverer claimed for palladium and sent samples for analysis to other chemists, all of whom reported that they could not check Chenevix' work. At about that time, 1804, Wollaston was ready also to announce the discovery of rhodium and to have himself known as the discoverer of palladium; the argument over palladium ended—as did, sad to say, the career of Chenevix as chemist.

After 1813 Wollaston busied himself with "equivalent weights," a term which he introduced. In a paper delivered before the Royal Society he defended his use of equivalent rather than atomic weights by saying that although chemical reactions are best explained by means of Dalton's atomic theory, yet for all practical purposes a consideration of equivalents is more important. So in preparing his Synoptic Scale of Chemical Equivalents he says, "I have not been desirous of warping my numbers according to an atomic theory but have endeavored to make practical convenience my sole guide."[5] This scale of equivalents made it possible to obtain results of calculations concerning equivalents quite mechanically. A table published in 1814 included values obtained by other chemists, such as Berzelius. Whereas Dalton had used as a standard for his weights H = 1, and Berzelius used O = 100, Wollaston selected O = 10. This was quite a complete table including equivalent weights of many elements and also of acids, bases, and salts. Wollaston's work did much to draw attention to Dalton's theory but also, unfortunately, helped considerably in confusing still further the minds of chemists in regard to the distinction between equivalent, combining, and atomic weights—a confusion which lasted until after the Karlsrühe meeting of 1860.

Wollaston, were he living today, would undoubtedly take an active interest in the field of crystal structure. More than one hundred years ago he wrote, "It is perhaps too much to hope that the geometrical arrangement of primary particles will ever be perfectly known—yet, until it is ascertained how small a proportion the primary particles themselves bear to the interval between them, it may be supposed that surrounding combinations, although themselves analogous, might dis-

[5] WOLLASTON, "A synoptic scale of chemical equivalents," *Trans. Roy. Soc.*, Nov. 4, **1813**, p. 7.

turb that arrangement, and in that case the effect of such interference must also be taken into account before any theory of chemical combination can be rendered complete."[6]

As officer in the Royal Society for many years, Wollaston knew either personally or by correspondence a great many chemists. Berzelius enjoyed his company on his visits to England. He helped to convert Sir Humphry Davy to Dalton's theory to which he himself readily subscribed, since it offered an explanation for the facts now stated in the Law of Multiple Proportions—facts that he realized but could not explain. He knew Faraday. He was one of the few with whom Cavendish was at ease. However, he was as cautious in forming friendships as he was in the statements he made. This extreme caution, combined with the fact that when he made a statement he knew it to be correct, gave him the nickname "The Pope." The friendships he did allow himself were warm and lasting. It seems that this great man, like Vauquelin, was never married.

[6] WOLLASTON, "On super-acid and sub-acid salts," Alembic Reprint No. 2, p. 40.

A Simple Wedge Type pH Colorimeter

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HYDROGEN ion concentration may be measured with indicators, without the need for separate color standards for each pH value, by means of a simple colorimeter constructed from two matched Erlenmeyer flasks. This device is an adaptation of the Bjerrum (*1*) wedge system which compares the test solution with the resultant color obtained at different positions along a pair of conjugate wedges containing the acid and alkaline modifications of the indicator, respectively. Wedge comparators have been previously described by Barnett and Barnett (*2*), Myers (*3*), McCrae (*4*), Exton (*5*), and Hellige (*6*).

DESCRIPTION

This instrument is essentially two juxtaposed wedges improvised by blocking off the conical volumes of an upright and an inverted Erlenmeyer flask with paraffin as shown in Figure 1. Into one central wedge-like space so formed is introduced the acid form of the indicator to be used; into the other wedge is placed the basic modification. The pair are stoppered and mounted, with their sloping sides contacting, in a wooden block suitably hollowed out for support. By viewing through the wedges a continuous color scale is seen, corresponding to pH variations. Stay wires, forming a collar and bridles, hold the flasks securely to the base. Due to curvature, the flasks contact only along a line, but the illusion of complete apposition across the full width of the window is obtained.

Paraffin is best poured into the flasks first on the sides, then on the bottom. Since paraffin shrinks on solidification, a depression left as each side cools must be filled out by a second pouring. The wedge space should have parallel sides and a horizontal bottom. Adhesion of paraffin may be improved by first roughening the surface of contact with the glass; however, no peeling or lifting of the paraffin mass from smooth clean glass had been noted after six months' use.

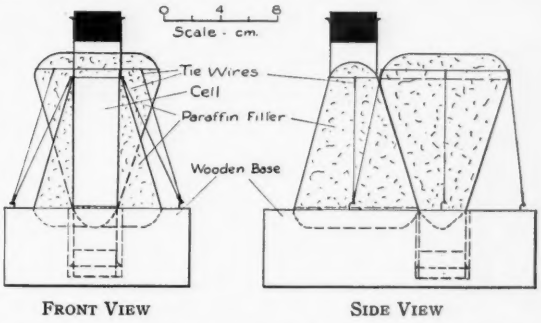

FIGURE 1.—WEDGE COLORIMETER MADE FROM TWO ERLENMEYER FLASKS

THEORY AND CALIBRATION

Since the dual wedge provides a liquid prism of constant total thickness the virtual color of the indicator forms, when looking through at any plane, will match that of a solution of equal effective indicator amount having the same fraction of each modification. The corresponding pH for any combination of acid and alkaline tautomers is given by the following fundamental expression, as shown in Clark's text (*7*):

$$\mathrm{pH} = \frac{1}{\log K_I} + \log \frac{\alpha}{1 - \alpha} \qquad (1)$$

where K_I is the apparent indicator dissociation constant and α the degree of color transformation, *i. e.*, the degree of dissociation for the monobasic acid type of indicator such as phenol red, or the fraction of undissociated residue for the monoacid base variety such as methyl red. If it is assumed for discussion that the simple monobasic acid type of indicator is employed, then α may be taken to represent the fractional thick-

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ness occupied by the alkaline tautomer at points along the wedge corresponding to pH values defined in equation (1).

If the preceding equation is differentiated with respect to the logarithmic function there results:

$$\frac{d\,\mathrm{pH}}{d\left(\log\frac{\alpha}{1-\alpha}\right)} = 1 \qquad (2)$$

from which the specific indicator constant has vanished. This expression shows that the plot of equation (1) on an abscissa scale of $\log\frac{\alpha}{1-\alpha}$ is a straight line of 45 degrees inclination for all simple indicators, provided unit distances along the axes are selected alike for both

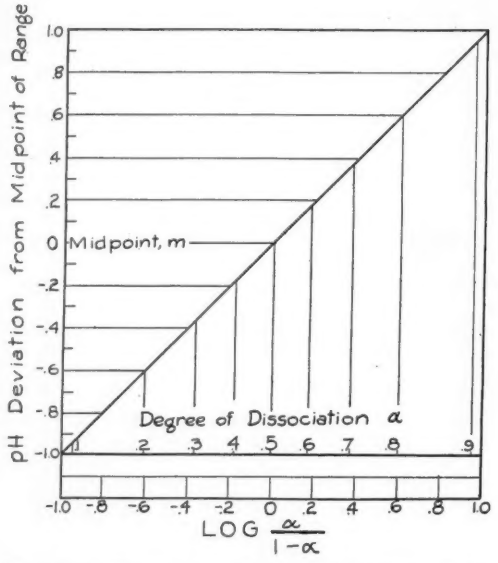

FIGURE 2.—GENERALIZED COLOR DEVELOPMENT PLOT FOR SIMPLE INDICATORS

pH and $\log\frac{\alpha}{1-\alpha}$ scales. In Figure 2 there are plotted in this manner generalized pH values, expressed as deviations from the median color, against the dissociation α. The abscissa is divided according to the function $\log\frac{\alpha}{1-\alpha}$ with corresponding values of α indicated on the graph for convenience. The plot passes through the characteristic mid-transformation point of the indicator where

$$\alpha = 0.50$$

and

$$\mathrm{pH} = \frac{1}{\log K_I}.$$

It may be well to point out that for the oppositely dissociating type of simple indicator, *i. e.*, monoacid bases, the log plot of Figure 2 would be a straight line of minus 45 degrees inclination.

Divisions along the window of the colorimeter are based on α spacings in Figure 2. Thus, for example, a pH value of 0.2 units less than the mid-color point is simulated where the dissociated fraction, or alkaline modification, is 0.39 of the total wedge thickness. If phenol red $\left(\frac{1}{\log K_I} = 7.7\right)$ is the indicator used, this position will give the color for pH 7.5.

The distance measured along the slant height of the wedge from the median point equivalent to any pH difference from the mid-transformation value of the indicator may be calculated directly from the formula:

$$d = \Delta\alpha \cdot s \cdot \frac{(b_1 + b_2)}{(b_1 - b_2)} \qquad (3)$$

where

d = distance from mid-point of wedge along slant sides
$\Delta\alpha$ = difference in indicator fraction dissociated from 0.50, corresponding to any desired pH deviation from mid-color point
s = slant height of wedge, from base to neck
b_1 = width of wedge at base
b_2 = width of wedge at neck

As an example of an actual calibration, values of α, corresponding to decimal pH increments, taken from Figure 2, are applied in equation (3) for the case of twin 300-ml. pyrex Erlenmeyer flasks having s = 9.2 cm.; b_1 = 8.7 cm.; and b_2 = 3.0 cm.

TABLE 1

CALIBRATION OF THE 300-ML. PYREX ERLENMEYER PAIR SHOWN IN FIGURE 1

ΔpH from mid-point	±0.0	0.1	0.2	0.3	0.4	0.5
Δα from 0.50	±0.0	0.057	0.113	0.167	0.215	0.26
d cm.	±0.0	1.1	2.1	3.2	4.1	4.9

If use of phenol red is intended, location of the pH increments shown in Table 1 are as follows:

TABLE 2

CALIBRATION OF WEDGE FOR PHENOL RED

pH	*d cm. from median*
7.2	−4.9
7.3	−4.1
7.4	−3.2
7.5	−2.1
7.6	−1.1
7.7	0.0
7.8	1.1
7.9	2.1
8.0	3.2
8.1	4.1
8.2	4.9

The acid modification is assumed in the upright flask.

The complete calibration equation of the wedge may be expressed by substituting the value of α from (3) into the fundamental indicator equation (1) to give:

$$\mathrm{pH} = \frac{1}{\log K_I} + \log\frac{0.5s(b_1 + b_2) + d(b_1 - b_2)}{0.5s(b_1 + b_2) - d(b_1 - b_2)} \qquad (4)$$

Equation (4) may be solved explicitly for departure from the median position for any simple indicator to give an exponential formula:

$$d = 0.5s\,\frac{(b_1 + b_2)}{(b_1 - b_2)}\left[\frac{K_I - 10^{-\mathrm{pH}}}{K_I + 10^{-\mathrm{pH}}}\right] \qquad (5)$$

which is not so convenient for calibration as is the graphical method based on Figure 2 and equation (3).

Due to the thickness of the neck of the flasks it is impossible to eliminate any one color variation entirely. This fact restricts the use of indicators to the central part of their range. If the biprism is constructed from two 300-ml. pyrex Erlenmeyer flasks, as in the above discussion the limiting values of α are 0.256 and 0.744, permitting the pH scale to cover slightly less than $\pm$ 0.5 pH units from the mid-transformation point. This useful zone falls somewhat short of the range provided by the usual commercial racks of buffer standards in test tubes, which generally reach $\pm$ 0.9 pH unit on either side of the mid-color value.

METHOD OF USE

A volume of indicator is placed in the sample held in any size ordinary test tube equal to that contained behind the same projected surface of the wedge. Thus if 5 ml. unknown solution containing 10 drops of indicator in the test tube is matched against a 300-ml. Erlenmeyer pair, these flasks should each contain 40 drops of indicator as calculated below:

For test tube:

Height of solution	3.3 cm.
Diameter	1.35 cm.
Volume of indicator selected	10 drops

For biprism:

Altitude of cell	9.0 cm.
Wedge width	2.0 cm.

Volume of indicator to be used in each flask

$$10 \times \frac{9.0}{3.3} \times \frac{2.0}{1.35} = 40 \text{ drops}$$

The test tube containing the sample and indicator is moved along the comparator until a color match is obtained and the corresponding pH is read directly off a calibrated scale constructed as previously explained. Comparison is facilitated by viewing the color scale through a horizontal slit in a paper shield.

Indicators which strongly exhibit the phenomenon of dichromatism should be observed through the same thickness of test sample as used in the wedges. For simple monochromatic indicators, the flask containing the colorless tautomer may in most instances be dispensed with.

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Consumer Education in the College Chemistry Course

HELEN I. MINER[1] Nazareth College, Nazareth, Michigan[2]

THE rapidly growing volume of consumer education material is proving valuable in the introductory college chemistry course. Two hundred seventy replies to a questionnaire sent in January, 1940, reveal the extent of its use in junior colleges and senior women's colleges.

The results of the survey are summarized in the accompanying table.

Examination of the table shows that proportionally more junior colleges than senior women's colleges supplement the introductory chemistry course with consumer education material. A small percentage of each group uses consumer chemistry as the main subject matter of the course. Replies to the questionnaire state that this is done only in terminal courses for students seeking a non-technical knowledge of chemistry.

TABLE 1

	Junior Colleges		*Senior Women's Colleges*	
	No.	*%*	*No.*	*%*
Replies to Questionnaire	220		50	
A. *Use Consumer Education Material*	123	55.9	23	46
I. Main Subject Matter	4	1.8	2	4
II. Background Material				
a. Whole course	56	25.5	11	22
b. Part of course	39	17.7	5	10
III. Very Limited Use	24	10.9	4	8
IV. Extent of Use Not Stated	0	0.0	1	2
B. *Do Not Use Consumer Education Material because:*	97	44.1	27	54
I. Prefer to Stress Principles	23	10.5	4	8
II. Not Applicable to a Pre-Professional Course	8	3.6	3	6
III. Material Considered in Other Courses				
a. Consumer Course	3	1.4	7	14
b. Not a Consumer Course	7	3.2	2	4
IV. Miscellaneous Reasons	24	10.9	2	4
V. Reason Not Stated	26	11.8	8	16
VI. Interested and Considering Its Use	6	2.7	1	2

[1] Present address: Wayne University, Detroit, Michigan.

[2] The mechanical aspects of making this survey were facilitated greatly by material assistance from Nazareth College.

When I was shown the Shell Company plant in California for the catalytic production of acetone and methyl ethyl ketone, which was carried out with the aid of a catalyst which I had discovered thirty-five years ago, the engineer who showed me the plant was absolutely sure that the Ipatieff who developed the process had been dead for quite some time.

—V. N. IPATIEFF

Chemistry Instruction for Purposes of General Education[1]

Report of A.A.A.S. Committee on the Improvement of Science Instruction for Purposes of General Education

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L. M. HEIL, *Research Assistant*, University of Chicago, Chicago, Illinois
P. E. SCHAEFER, *Research Assistant*, Ohio State University, Columbus, Ohio

THIS report represents one phase of a study undertaken by a special committee of the American Association for the Advancement of Science on the improvement of science teaching.[2] The attention of this special committee was to be devoted mainly to the problem of improving science instruction in colleges and universities for the purposes of general education. The committee has assumed the following two responsibilities as an initial attack on the problem:

(1) To make a study of the current instructional practices in those courses which are designed primarily for purposes of general education; that is, those courses designed for students who take but few courses in science and for whom such courses are terminal.
(2) To determine those experimental studies which seem to be the most important and urgent to be carried on with the aim of improving science instruction for the non-scientist.

The committee, therefore, in attacking the problem decided that some effort should be made to determine the point of view of science teachers with respect to certain issues involved in this question and also to discover the present practices in those courses designed primarily for purposes of general education. The committee decided that a first step might be that of obtaining certain of this information by means of a questionnaire.

THE PURPOSES OF THE QUESTIONNAIRE

The purposes of the questionnaire were twofold:

(1) To obtain the reactions of science teachers concerning some of the issues involved in the problem of science for purposes of general education.
(2) To locate those science departments which have given considerable thought to and which have had considerable experience with courses designed for the non-scientist.

The questionnaire concerning the instruction of chemistry for purposes of general education was sent to approximately 500 colleges and universities. The returned questionnaires were distributed among the various types of colleges and universities in the following way:

158—colleges and universities
38—teachers colleges
15—professional colleges

About half of the questionnaires were answered by the head or chairman of the department of chemistry. Thirty-six per cent were answered by individuals with the rank of full professor in the department of chemistry, while 16 per cent were answered by persons holding the rank of associate professor or lower. One of the questionnaires was answered by a committee of teachers within the department.

Four major themes or questions were incorporated into the questionnaire:

(1) What are the opinions of chemistry teachers concerning some of the important issues in the problem of chemistry instruction for purposes of general education?
(2) What do chemistry teachers believe should be accomplished in a chemistry course for the non-science student?
(3) What has been done by various chemistry departments in an attempt to meet this problem?
(4) What are some of the major problems to be solved if chemistry instruction for the non-science student is to be improved?

Only those most frequently mentioned and discussed issues and problems were included, so that the questionnaire would be as short as possible and the response would be large. Additional comments were invited and many teachers expanded their answers to the questions with several pages of written comments.

[1] A preliminary report of the special committee of the American Association for the Advancement of Science on the improvement of science teaching in colleges and universities. This committee is made up of representatives from each of the following science fields: physics, mathematics, chemistry, botany, zoölogy, and the earth sciences (geology and geography).

[2] *Science*, **87**, 454 (1938).

THE QUESTIONNAIRE AND THE RESULTS

In preparing the questionnaire specific questions were formulated to obtain information concerning the more general questions or items stated above. The questionnaire and the response to it by 211 chemistry teachers is given in the following table:

A relatively small number of the students who enter the introductory course in college chemistry continue their study in more advanced courses. A larger group of students take the course in order to meet certain requirements and still another group take the course solely for its contribution to their general education. The assumption has usually been made that essentially the same type of introductory chemistry course meets the needs of these different groups of students. One of the questions of general concern which this Committee believes should be studied may be phrased as follows: Does the conventional introductory college course in chemistry through its content and method of instruction make a larger contribution to the education of those students who do not continue the study of the subject than would be possible in a different type of course?

The Committee would appreciate your coöperation in answering the following questions related to the problem above. The Committee makes no pretense that this questionnaire is complete and you may wish to add comments on the reverse side of these sheets related to the questions or to add other questions which are not presented in the questionnaire.

A. Do you consider that the conventional introductory college course in chemistry as represented by a majority of current textbooks and laboratory manuals:

	The response of 211 teachers answering the questionnaire		
	Yes	*No*	*Uncertain*
1. Is in general satisfactory for the non-specializing student?.....	65	122	22
2. Is more appropriate for students who later specialize in chemistry than for those who do not?	153	34	13
3. Could be significantly improved for the non-specializing student?.....	137	35	38
4. If modified for the non-specializing student would be in danger of becoming superficial?.....	108	56	39
5. Should be replaced for the non-specializing student by a physical science survey course?....	34	107	60
	Yes	*No*	*Uncertain*
Do you consider that:			
6. The time and cost involved are essential factors which have tended to retard the introduction of courses designed to meet the needs of the non-specializing student?.....	97	79	32
7. The emphasis placed on "pure research" as a basis for advancement of the instructional staff has retarded the development of a real concern about, and research upon teaching problems related to general introductory courses in chemistry?.....	148	36	29

B. What do you believe are the most significant contributions which a study of chemistry should make for those students who are not to specialize in chemistry? (Indicate by the number 1 if you believe the contribution to be very important; by the number 2 if you believe the contribution to be of some importance; by the number 3 those contributions which a chemistry course should not attempt to make.)

The course should:	*1*	*2*	*3*
1. Develop the ability to do critical thinking.....	176	26	9
2. Show how the discoveries of science have contributed to the solution of some problems of living and have created others..	138	70	1
3. Show how certain social prejudices have retarded the application of science discoveries in problems of everyday living...	24	124	55
4. Develop the ability to treat quantitatively problems as they are usually treated in chemistry textbooks.....	32	104	71
5. Develop certain manipulative skills involved in laboratory technics.....	44	96	66
6. Expand the interests of students by encouraging hobbies and outside activities which are related to chemistry.....	49	117	40
7. Make students familiar with the facts, principles, and concepts of chemistry.....	151	53	3

C. If your department has made some change in the introductory course in the last five years, what direction has it taken?

	Yes	*No*	*Uncertain*
1. Has the content and program of instruction been considerably modified within the framework of the old course?.....	122	51	5
2. Has the department replaced an old course with a survey course?.....	16	156	2
3. Has the department introduced new courses (such as survey courses) in addition to the regular introductory course?...	73	107	..
4. Do you rely mainly upon a single textbook and laboratory manual in the new or revised course?.....	101	55	2
5. Are you using an outline or syllabus which you have prepared especially for the new course?..	35	95	1
6. Do you attempt to treat most of the traditional content such as the study of gases, metals, nonmetals, etc., as separate units in the revised course?.....	47	80	5
7. Do you expect more outside readings in a survey course than you do in a course designed primarily for further work in chemistry?.....	67	41	11
8. Is the work in the new or revised course carried on independently of other physical science courses such as physics, astronomy, or geology?.....	98	33	1
9. Has your department prepared a bibliography of reading materials related to the interests of those people who may not specialize in chemistry?.....	46	108	4
10. Has your department prepared a list of problems requiring investigations which can be carried on by the student outside of the classroom and laboratory?.....	14	143	4

11. Has your department prepared special tests or other means of evaluating student achievement of the distinctive aims for the new or revised course?....	31	118	..

D. What are some of the things which you would like to have developed in a further consideration of the problems stated above? (Indicate by the number 1 those things which you believe to be very important; by the number 2 those which you believe have some importance; and by the number 3 those which you believe are not at all important for this problem.)

	1	*2*	*3*
1. The clarification of a point of view for teachers of science with respect to the place of science (and especially chemistry) in general education at the college level.....	149	41	6
2. The preparation of a list of problems suitable for purposes of general education which require:			
(*a*) Investigations making use of library materials.....	101	83	13
(*b*) Investigations requiring experimentation outside the laboratory.....	39	83	60
(*c*) Investigation in the laboratory.....	81	77	33
3. The preparation of reading material designed:			
(*a*) To develop the ability to see the implications of the discoveries and inventions of science for everyday living.....	147	45	8
(*b*) To encourage thinking as to how to overcome those prejudices which have retarded the application of scientific discoveries for the importance of everyday living.....	80	94	23
4. The preparation of a bibliography of reading designed for purposes of general education suitable for use in chemistry courses.....	119	71	12
5. The development of methods for discovering the particular needs and interests of students and for selecting content and teaching procedures to meet those needs and interests.....	123	54	18
6. The preparation of tests designed to measure the achievement of students with respect to certain aims generally not now specifically tested, such as understanding and use of the "scientific method" and the ability to do clear thinking....	118	59	23
7. The development of technics for interpreting and using test results for the purpose of improving the achievement of students.....	94	69	29
8. The training of those people already engaged in the teaching of chemistry to meet the problem of chemistry in general education.....	127	61	12
9. The institution of graduate courses, such as history of chemistry and philosophy of science, taught by scientists in graduate schools.....	60	87	42

ANALYSIS AND INTERPRETATIONS MADE OF THE RESULTS

The response to Part *A* of the questionnaire indicates that the majority of the chemistry teachers answering the questions believe the introductory course in chemistry to be unsatisfactory for the student who will not specialize in science. They believe the regular course could be significantly improved for the non-specializing student, but they also believe that modification of the regular course may lead to superficial results for the specializing students. The group as a whole seems quite definitely opposed to replacing the conventional introductory course in chemistry by a physical science survey course for the non-specializing student. (Supplementary comments seem to indicate, however, that many of the instructors reacted negatively to "survey" courses. Instructors do seem to feel that an additional course should be provided, but not the type of course commonly known as a physical science survey.) There is general agreement that the emphasis placed on "pure research" as a basis for advancement of the instructional staff has retarded the development of a real concern about and research upon teaching problems related to the general introductory courses in chemistry.

Additional comments on Part *A* of the questionnaire reveal that chemistry teachers are much concerned about the possibility of superficiality in the introductory chemistry course for the non-specializing student. This is expressed very well in the following quotation:

"My one fear is that the course will become too superficial so that students get no more of value from it than they would be reading a popularizing book on chemistry. If the chemistry is too 'candied,' the student does not acquire a familiarity with the work of the chemist and may be misled into believing himself specially fitted for a career in chemistry—many students who select the less technical courses do so in the belief that they will be 'easy'—unfortunately this often is true and the students learn habits of laziness and often even of inaccuracy..."

Several comments stressed the point that the introductory chemistry course could be improved for the specializing as well as the non-specializing students. One instructor suggested that "Improvement could be made by more emphasis on topics more closely related to daily life—especially for the girls."

Most comments were made on Question *A*-5 (the introductory college course in chemistry should be replaced for the non-specializing students by a physical science survey course). Some of these comments were:

"Depends on the survey course."

"Physical science survey course should be followed by a chemistry course."

"Would have both groups take a fundamental course in science, but would separate the two groups because of different interests, abilities, and training."

"Is this attempted in all other fields of learning?"

"The introductory course often leads students to specialize in this field; this would not be the case if they took a survey course."

"Necessary to teach the underlying principles and theories of chemistry because of the number of the students who take the course as a requirement and then decide to take advanced work."

"Segregation of specializing and non-specializing students at other places—not in the elementary courses."

The purpose of Part *B* of the questionnaire was to obtain the beliefs of chemistry teachers concerning the contributions or purposes of chemistry instruction for the student who is not specializing in sciences. Respondents to the questionnaire were most in agreement that *B*-1 (the course should develop the ability to do critical thinking) is the most important aim of the introductory chemistry course for students who are not specializing in chemistry. They also regarded *B*-7 (the course should make students familiar with the facts, principles, and concepts of chemistry) and *B*-2 (the course should show how the discoveries of science have contributed to the solution of some problems of living and have created others) as being very important. The other four aims listed were regarded as being of some importance.

A number of comments on the aims listed in Part *B*, although not numerous, present interesting sidelights. For question *B*-1 (the course should develop the ability to do critical thinking) the following comments were made:

"Claimed as an outcome of most any kind of science course."

"Important, but not developed by the courses as usually taught."

"May give practice in critical thinking, but *develop* it?"

The comments on *B*-7 (the course should make students familiar with the facts, principles, and concepts of chemistry) suggested that the students should be familiar, but not expert, in the use of these facts, principles, and concepts; and that only sufficient factual material should be introduced to unify and develop the principles.

The questions of Part *C* were designed to obtain evidence concerning present practices utilized in courses primarily for the non-specializing student. Almost 65 per cent report that the content and program of instruction has been considerably modified within the framework of the old course, 41 per cent report that the department introduced new courses (such as survey courses) in addition to the regular introductory courses, while only 9 per cent report that the department has replaced an old course with a survey course.

Of the institutions reporting change, 72 per cent report changes in *C*-1 (the content and program of instruction has been considerably modified within the framework of the old course); 51 per cent, changes concerned only with *C*-1, while 18 per cent involve changes in both *C*-1 and *C*-3 (the department has introduced new courses—such as survey courses—in addition to the regular introductory course). The evidence suggests that few sweeping changes have been made. Instead changes seem to be either a modification of the existing program or the addition of a new course. Occasionally, both modification of the existing program and introduction of a new course takes place. Seldom is the old course replaced by a new course.

While 63 per cent of the teachers rely mainly upon a single textbook and laboratory manual in the new or revised course (*C*-4), 56 per cent expect more outside readings in a survey course than they do in the course designed primarily for further work in chemistry (*C*-7). Twenty-seven per cent of the instructors are using outlines or syllabi which they have prepared especially for the new course (*C*-5). About 39 per cent attempt to cover the traditional content in the revised chemistry course (*C*-6). Question *C*-8 (Is the work in the new or revised course carried on independently of other physical science courses such as physics, astronomy, or geology?) furnishes further evidence that the survey course, especially the survey course which combines chemistry with other physical science courses, is offered in 25 per cent of the colleges.

Increasing use of the library is suggested by the fact that 29 per cent of the instructors report that the department has prepared a bibliography of reading materials related to the interest of those people who may not specialize in chemistry (*C*-9). The response to the questionnaire seems to indicate that little use is made of the students' time outside of the classroom and laboratory for investigation of problems. The need for more adequate testing in the new or revised courses is suggested by the fact that only 21 per cent of the questionnaires indicated that steps had been taken for evaluating student achievement.

A number of the comments on this section of the questionnaire indicated that survey courses had been tried and then dropped because they attracted the poorer students, attracted very few students, or the students expected "snap" courses. Other obstacles were (1) difficulty in getting well-trained men to teach the survey courses, (2) difficulty in getting the type of textbook wanted, or (3) the difficulty in getting close coöperation between the instructors in the various science departments.

In Part *D* of the questionnaire an attempt was made to determine the opinions of chemistry teachers concerning the importance of certain projects which, if adequately developed, might increase the effectiveness of chemistry instruction for the student not specializing in chemistry.

Of most importance to these teachers is *D*-1 (the clarification of a point of view for teachers of science with respect to the place of science—and especially chemistry—in general education at the college level). Referring to Question *A*-1 it may be seen that the majority of teachers do not feel that the introductory college course in chemistry is in general satisfactory for the non-specializing student. The interest of teachers in this project seems to indicate that a general uncertainty exists concerning what chemistry instruction should do for the non-specializing student. The large proportion of the instructors, who regard "critical

thinking," appreciation of the discoveries of science, and familiarity with the facts and principles of chemistry as the most important outcomes for the non-specializing students, seems to suggest a need for further analysis. Such analysis might include suggestions concerning the following questions: "What is meant by critical thinking in the field of chemistry?", "What is meant by understanding a chemistry principle or concept?", "What are some of the criteria which would enable a chemistry teacher to select and justify the inclusion of certain chemistry principles and concepts in his program of instruction?"

The project *D*-5 (The development of methods for discovering the particular needs and interests of students and for selecting content and teaching procedures to meet those needs and interests) ranked fourth in importance, according to the judgment of these teachers. Many of the problems involved in this project are inextricably related to the problem of formulating a point of view concerning science in general education, while others relate to experimental studies. For example, one assumption which represents a trend in chemistry instruction for the non-specializing student is that the learning experiences are more effective through demonstrations and lectures rather than through individual experimentation and discussion. A number of chemistry teachers have expressed a desire for experimental evidence concerning this assumption so that they would be able to carry on more effective instruction in their courses.

At least three of the projects, *D*-3*a*, *D*-4, and *D*-6, represent assistance which many departments desire. Just how this assistance could be provided is a question, but it appears that these projects all involve problems which are interrelated and an arrangement, possibly that of a central committee or staff working closely together on these problems, would constitute one way of getting answers to some of the problems as well as that of having teaching materials developed which would be helpful to teachers.

POINTS OF VIEW CONCERNING CHEMISTRY INSTRUCTION FOR PURPOSES OF GENERAL EDUCATION

The responses of chemistry teachers to the questionnaire seem to fall into two general categories representing opposite points of view concerning whether the typical course in chemistry is adequate to meet the needs of the student who is not specializing in science. Within each of these two categories, however, there are several rather distinct differences.

That the Method and Content of the Regular Introductory Course in Chemistry Is Satisfactory for the Non-specializing Student (73 in This Group)

Seventy-three persons who answered the questionnaire indicated rather clearly that they believe the present regular introductory course in chemistry to be satisfactory for the non-specializing student. Of this group, 29 indicated that some modifications of the introductory course had taken place in their institution; 13 indicated that the department had introduced new courses (such as survey courses) in addition to the regular introductory course; 7 indicated that both a modification of the regular course and the introduction of a new course had occurred; one indicated modification of the regular course, replacement of an old course with a survey course, and the addition of a new course; and 23 reported that their department had made no significant changes in the last five years. It is possible that the majority of this group who believed the introductory chemistry course to be satisfactory for the non-specializing student were responding to the question as it applied to their own institutions—where changes had taken place—rather than to the condition in other institutions as seen by the adoption of textbooks and laboratory manuals.

That the Method or Content of the Regular Introductory Course in Chemistry Is Not Satisfactory for the Non-specializing Student (136 in This Group)

(*a*) One hundred nineteen persons answering the questionnaire indicated that they believed the regular course does not now meet the needs of the non-specializing student but could be significantly improved. Of this group, 31 are also afraid that modification might lead to superficiality, while 21 would replace the introductory chemistry course by a physical science survey course for the non-specializing student.

(*b*) Six of the persons answering the questionnaire indicated that they believed the regular chemistry course does not meet the needs of the non-specializing student but are afraid that modification may lead to superficiality. Two of the group, in spite of their fear of superficiality, would replace the regular course with a physical science survey course for the non-specializing student.

(*c*) Five of the persons answering the questionnaire believe the regular course does not meet the needs of the non-specializing student and would replace it by a physical science survey course.

(*d*) Six of the persons answering the questionnaire are dissatisfied with the introductory course in chemistry but offer no solution.

The above report represents an attempt to summarize the returns of the questionnaire to college chemistry teachers. The report may serve to provide some evidence concerning the feelings and opinions of a large number of chemistry teachers on the problem of chemistry for purposes of general education. The committee will present a formal report to the executive committee of the American Association for the Advancement of Science in which it will attempt to summarize its opinions concerning possible steps to take in the attack of certain of the problems pertaining to the improvement of science instruction for purposes of general education.

Some Lecture Demonstrations[1]

FREDERIC B. DUTTON[2]
Baldwin-Wallace College, Berea, Ohio

1. BOYLE'S LAW

MOST apparatus for the demonstration of Boyle's law requires the observation of volumes of gas in a small tube visible to the demonstrator but not to the student in the last row. The apparatus herein described is designed to demonstrate visibly to each member of the class the principle as simply and forcefully as possible.

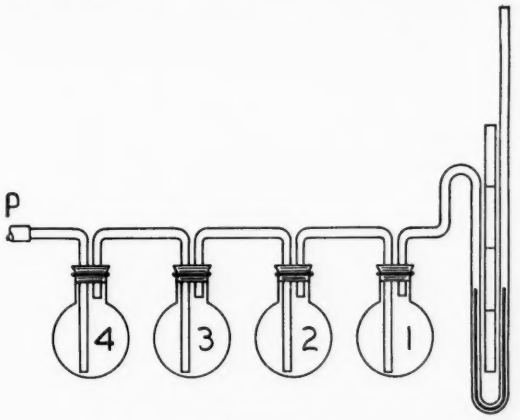

FIGURE 1

The apparatus shown in Figure 1 consists of four one-liter flasks fitted with two-hole rubber stoppers wired in place, and is connected as shown with an open mercurial U-shaped manometer. The connections are of 7-mm. glass tubing.

In use, the system is evacuated with a pump (Hyvac or filter pump) connected at *P* to demonstrate atmospheric pressure (Figure 2). Comparisons may be made with the usual types of barometers. Air is then admitted by disconnecting the pump. The system now consists of four liters of air under a pressure of one atmosphere (Figure 1). A connection is now made with the water supply at *P* and water admitted until the first flask is full (Figure 3). The system now contains three liters of air under a pressure of one-third of an atmosphere more than the air in the surrounding room or one and one-third atmospheres. In a similar manner the second flask is filled with water and the system then contains two liters of air under a pressure of two atmospheres (one more than normal atmospheric pressure) (Figure 4). It is immediately apparent that the volume has been halved and the pressure doubled. If the final step were to be taken and the third flask filled with water the system would consist of one liter of air at a pressure of four atmospheres. This last step is not

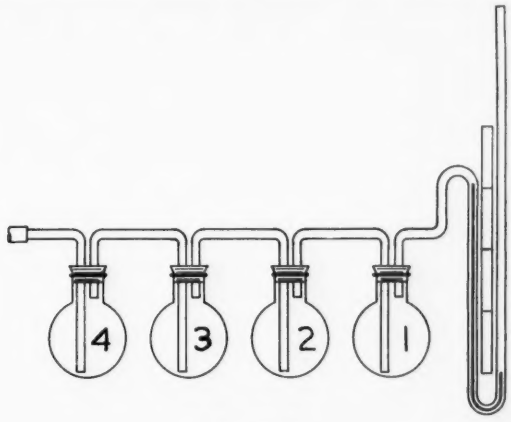

FIGURE 2

advisable because it is difficult to wire the stoppers in securely enough to withstand the pressure; the manometer must be made too high for convenience in handling; and there is danger from flying glass if the flask

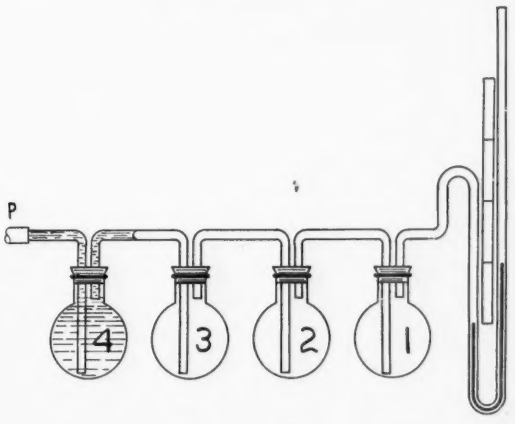

FIGURE 3

should be broken.[3] If this last step is taken a shield

[1] Presented before the Division of Chemical Education at the ninety-sixth meeting of the A. C. S., Milwaukee, Wisconsin, September 7, 1938.

[2] Present address: Eaton Rapids, Michigan.

[3] The author has repeatedly subjected several flasks to a pressure in excess of five atmospheres without once having a flask break. When a flask was purposely broken with a hammer a forceful explosion took place.

should be provided to protect the class and demonstrator if the flask should fail.

Many variations will suggest themselves. If the demonstrator prefers, a closed tube manometer may be used, in which case it must be correspondingly taller. The demonstration may be repeated starting with one-half atmosphere of air in the four flasks. It should be emphasized that the pressure indicated by an open-end manometer is in addition to or above the atmospheric pressure. A measuring stick is used which is calibrated in thirds of an atmosphere (25, 50, 75, and 100 cm.) and may be compared with the usual meter stick to convert to mm. or cm. of mercury. It should be

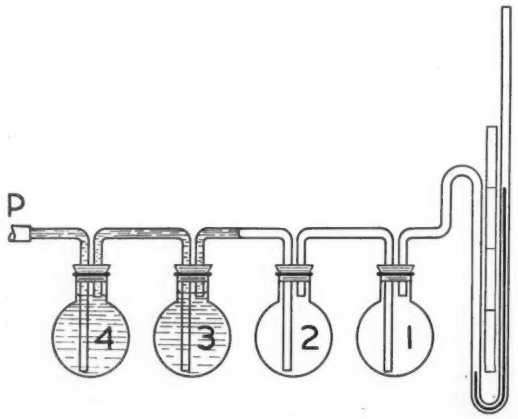

FIGURE 4

further pointed out that these are rough measurements to illustrate a principle. More precise technic would require corrections for the volume of tubing, calibration of flasks, partial pressure of water vapor, and would show the irregularities caused by a departure from the perfect gas law. The enumeration of these sources of error may be used as an assignment to interest those who have had previous training in chemistry or physics, while demonstrating the fundamental principle to those who have not had such training.

With this apparatus all measurements are visible from any part of the lecture room and yield the following simple values, easily checked mentally by any student.

$$\begin{aligned} P \times V &= PV \\ 1 \times 4 &= 4 \\ 1^1/_3 \times 3 &= 4 \\ 2 \times 2 &= 4 \\ (4 \times 1) &= 4 \end{aligned}$$

2. CHANGE OF STATE

Several demonstrations of the transformations of energy accompanying changes of state have been described in this JOURNAL,[4] and elsewhere. A simple

[4] HOLMES AND SNODDY, J. CHEM. EDUC., **8**, 1166 (June, 1931); HAUBEN, *ibid.*, **9**, 1115 (June, 1932); MARKLEY, *ibid.*, **11**, 251 (April, 1934).

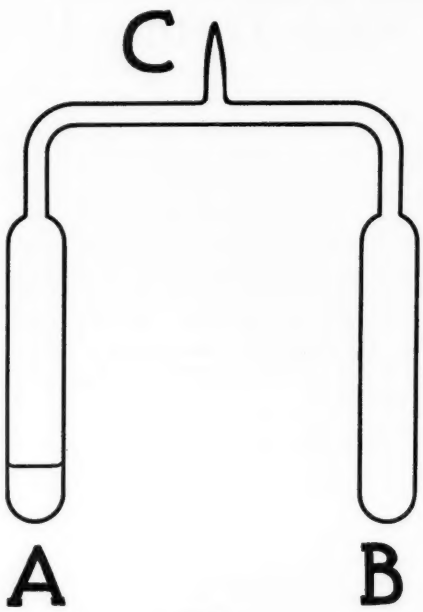

FIGURE 5

demonstration of change of state is accomplished with the aid of the apparatus shown in Figure 5. It is a modification of the Cryophorus shown in physics apparatus catalogs and consists of two ampoules drawn down from one-inch test tubes and connected with 7-mm. glass tubing. A short side arm is sealed in as

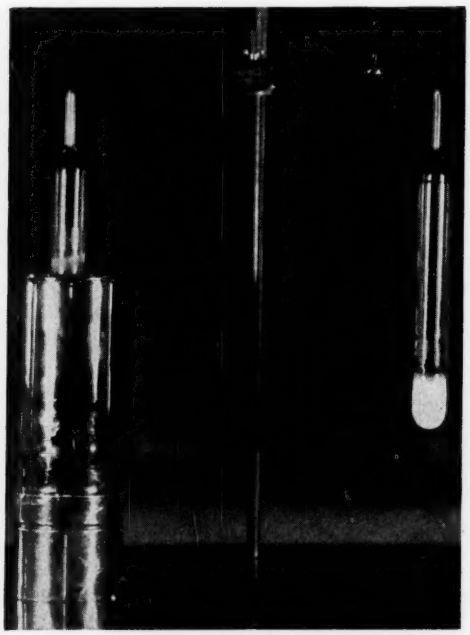

FIGURE 6

indicated at *C*. About 20 ml. of ether are introduced through the side arm and distributed equally between the two ampoules. The system is then partially evacuated by connecting to the aspirator or water pump. This causes the ether to boil violently, sweeping out the air. The boiling is continued for about a minute; then the rubber connection to the pump is closed with a screw clamp and the side arm is sealed off.

In use, all of the ether is poured into one of the ampoules and the other surrounded either by liquid air or by an acetone–dry ice mixture. The ether vapor is condensed in the cold ampoule, the pressure in the system is reduced, and the liquid ether boils rapidly. Within a few minutes a thick layer of frost has formed on the bottom of the ampoule containing the boiling ether, giving visual evidence that heat is being absorbed from the walls of the tube and the surrounding atmosphere (Figure 6).

Comparisons may be made between this simple device and the artificial refrigerator, a steam heating plant, or any distillation or evaporation process. In drawing an analogy to the artificial refrigerator it must be pointed out that to complete the cycle a pump (or absorption cycle) is used which reduces the pressure in the cooling unit *A* in the refrigerator box, compresses the gas which gives up its heat at a higher temperature to the room through a radiator *B*, liquefies, and is returned to *A* through a valve. In a steam-heating plant, *A* represents the furnace boiler where heat is introduced, the liquid vaporized and passed to the radiators; *B*, where the heat is given to the room and the vapor condensed. The return in this case is either by gravity or a pump.

This apparatus becomes a permanent piece of lecture demonstration equipment. It never needs adjustment, is instantly ready for service, and the demonstration is complete within three to five minutes—less time than it takes to tell about it.

A Mathematics Test as a Chemistry Placement Test

OMAR C. HELD

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THE University of Pittsburgh chemistry department offers two general inorganic chemistry courses for the University students. One of these courses is designed for students who have had high-school chemistry, and the other for those who have not.

This method of admitting students to the more advanced course in inorganic chemistry has not been entirely satisfactory to the chemistry staff. The fact that a student has presented a unit of high-school chemistry is not a good index of his ability to function satisfactorily in the more advanced inorganic course. Some students do quite well, while others are incapable of doing the work in this course, and should probably be enrolled in the course with those who have not had high-school chemistry.

In view of the present unsatisfactory method of placing students in chemistry, the staff members have been looking about for a better placement technic. They feel that a chemistry placement test would not quite meet the situation, as the students' inability to function satisfactorily in the course is due fundamentally to a weakness in mathematics.

At the present time, the University is giving a mathematics placement test to all freshmen who expect to take mathematics. The author wondered if this test could not also be used for a similar purpose for chemistry.

A group of 269 engineering freshmen who entered the University over a period of three years, who were placed in this more advanced inorganic chemistry on the basis of their having had a high-school course, and who had also taken the mathematics placement test, were selected for study.

We are primarily interested in finding which of these students should have been placed in the course with those students who had had no high-school chemistry. It was assumed that those who made "D" and "F" grades in the first semester of the more advanced inorganic chemistry course had poor preparation for the course. It was also assumed that those who did "C" grade of work had a fair background for the course, and those who made "A" and "B" grades had good preparation.

The mean mathematics placement test score was computed for each group, that is the "D, F" group, the "C" group, and the "A, B" group. Tables 1 and 2 summarize the data.

TABLE 1

MATHEMATICS PLACEMENT SCORES OF STUDENTS IN THE MORE ADVANCED INORGANIC CHEMISTRY COURSE IN THEIR FIRST SEMESTER

Chemistry Grade	*Number of Students*	*Mean Mathematics Placement Score*
A or B	104	35.31
C	82	30.70
D or F	83	27.00

TABLE 2

RELIABILITY OF THE DIFFERENCES OF THE MEANS OF THE THREE GROUPS

Grade Group	*Actual Difference*	*Reliability of Difference*	*Difference* *Reliability of Difference*
(A or B) – (C)	4.61	1.00	4.61
(A or B) – (D or F)	8.31	1.02	8.15
(C) – (D or F)	3.70	1.13	3.27

In each instance there is a statistically reliable difference between the groups. This would seem to indicate that our mathematics placement test might be used as a chemistry placement test to good advantage.

Water: Some Interpretations More or Less Recent[1]

GEORGE S. FORBES

Harvard University, Cambridge, Massachusetts

THE fundamental importance of water is reflected in the vast literature relating to it. For instance, the index of *Chemical Abstracts* for 1939 lists over 1200 water references. Dorsey's recently published compendium, "Properties of Ordinary Water Substance," restricts itself to 700 pages only by severe limitation of the topics to be discussed. Recent research is centered largely upon heavy water, D_2O^{16}, but no doubt H_2O^{18} and D_2O^{18} will have their turn later. The theoretical treatment of water, long stagnant, is now advancing toward prediction of its physical constants and behavior, starting from fundamental considerations.

Water is by no means a typical liquid; indeed, its properties verge upon the grotesque. Yet most students, up to the end of sophomore year at least, think of bromine, carbon tetrachloride, and mercury, rather than water, as exceptional liquids. Few chemical curricula ever undertake a systematic and connected discussion of water at any academic level. Only a week's study at the very beginning, and then isolated driblets as the exigencies of subsequent situations may require. Classical pictures, only, until the students' mathematical and physical knowledge suffices for technical discussions of recent data and theories.

I do not advocate total war upon the conventional order of presentation. None the less it is a pity that so many fruitful ideas should be segregated in advanced books and advanced courses if it is really possible to make them intelligible and useful at some earlier stage of the educative process.

THE FORMATION OF WATER

The elementary student is too often told that two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. If so, his first and therefore most enduring picture of a reaction mechanism is a preposterous one, which he will instinctively carry over to other reactions as well. The actual reaction scheme is of course immensely complicated, and not even now entirely agreed upon in all its details. It is clear, however, that hydrogen atoms and oxygen as well as free hydroxyl radicals are indispensable as intermediaries. The very simplest scheme is represented in Figure 1. After the initial reaction the hydrogen atom, only, is capable of initiating further reaction. But in the second stage we have two chain carriers, OH and O, and in the third stage three. In the fourth there will be five and in the fifth eight. From then on, the number of chain carriers will increase very rapidly, on paper at least, even without taking account of rising temperature. Such a mechanism is called a branching chain reaction, and accounts for the explosive properties of this and many other gas mixtures.

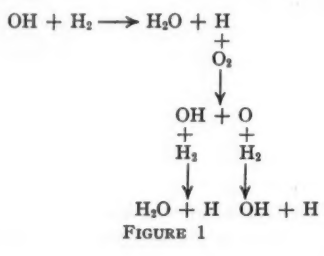
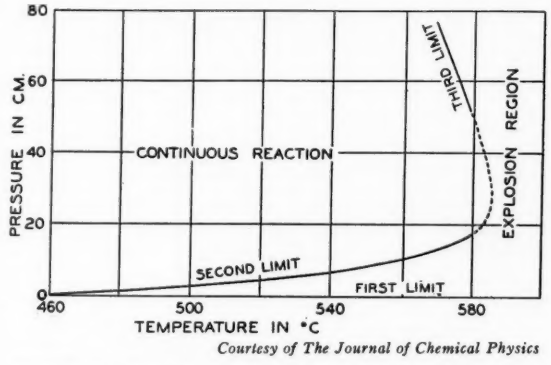


FIGURE 1



Courtesy of The Journal of Chemical Physics

FIGURE 2.—EXPLOSION CONDITIONS FOR HYDROGEN AND OXYGEN IN THE VOLUME RATIO 2:1

Most students jump to the conclusion that hydrogen-oxygen mixtures infallibly explode when heated, unless perhaps the pressure is very low. Yet even when mixed in the volume ratio 2 : 1, there is a wide range of conditions over which no explosion occurs. The diagram (Figure 2) was published by Oldenberg.[2] The explanation seems to be that the chain carrying hydrogen atoms can collide with oxygen molecules either on the walls of the vessel or in contact with a third molecule in the gas phase to form the inefficient free radical HO_2. In the region of slow reaction, chain carriers are being eliminated by chain-breaking reactions as fast as they are formed. But outside that region the chain-carrying reactions get out of hand so that an explosion occurs. For instance, a mixture in the ratio 2 : 1 at 570°C. and 300 mm. could be made to explode by either raising or lowering the pressure enough to cross the boundary between the two regions.

From this scanty picture of water formation it can

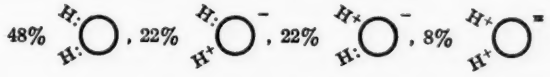
[1] Presented before the Second Summer Conference of the New England Association of Chemistry Teachers, Orono, Maine, August 12–16, 1940.

[2] OLDENBERG, *J. Chem. Phys.*, **8**, 469 (1940).

be inferred that most chemical reactions are much more complicated than their stoichiometrical representations, and that atoms or unsaturated radicals are likely to be involved in many of them. A vast amount of research is in progress upon this type of problem.

STRUCTURE OF THE WATER MOLECULE

Many of the properties of water have become intelligible since 1932, when Mecke[3] analyzed the absorption spectrum of water, and showed that its molecule is triangular. The bond angle between the lines connecting the hydrogen nuclei with the oxygen nucleus is about 105°. The OH distance is 0.99 A. (1 A. = 10^{-8} cm.) and the radius of the molecule, 1.38 A., is only slightly greater than that of the oxide ion, namely 1.35 A. The hydrogens are deeply imbedded in the oxygen atom so that the molecule is approximately spherical. This structure results in an uneven distribution of charge in the molecule. An excess of positive charge appears at or between the protons, and the opposite end of the molecule is negative, with perhaps some tendency for the excess of negative charge to be concentrated at two points so located that they and the two protons form the corners of a tetrahedron. Thus water is a dipole. A contributing factor seems to be the mixed character of the bonding. The properties of the molecule suggest that the bonds are not purely covalent but have a tendency to be ionic. That is, the electron pairs tend to draw away from the protons to form one or two hydrogen ions held to the negatively charged oxygen by a force approaching ordinary coulombic attraction. Pauling[4] has argued that four structures must be included in the picture as follows:



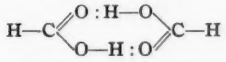
This idea of mixed binding should be applied quite generally in both inorganic and organic chemistry. If one writes a single cut-and-dried electronic formula for an inorganic compound, one would say at the most that the structure represented is the predominant one. Today an indispensable task of inorganic chemistry is to estimate the relative importance of the various probable structures.

WATER AS A LIQUID

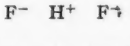
Normal liquids, such as Br_2, CCl_4, or Hg would doubtless be close-packed aggregations of molecules, like shot in a bottle, were it not for the thermal motion which expands and distorts such a configuration more and more as temperature rises. Such liquids owe their cohesion to the weak van der Waals forces between individual molecules. Their latent heat of vaporization, L, can be predicted from Trouton's rule; $L = 21\ T_b$ calories per mol where T_b is the absolute boiling point under atmospheric pressure.

Water, however, belongs to the so-called associated liquids, though not in the sense that it forms discrete groups of two or three molecules each as was once supposed. Other examples are HF, H_2O_2, and HCN. All these molecules contain a highly polar group, $\overset{-}{O}\overset{+}{H}$ or $\overset{-}{F}\overset{+}{H}$ or $\overset{-}{C}\overset{+}{H}$. The mutual attraction of these dipoles makes the cohesive forces much greater than if van der Waals forces only were involved. Yet even in this peculiar group, water is unique, as will appear from the following considerations.

If water or ice were made up of close-packed spherical molecules having a radius of 1.38 A., the density would have to be 1.84 instead of 0.91 and 1.00 respectively. But X-ray examinations of ice and water by Bernal and Fowler,[5] Katzoff,[6] Morgan and Warren,[7] showed that each water molecule tends to coördinate four other molecules around it so that the centers of the four coördinated molecules lie at the corners of a tetrahedron. This pattern tends to be repeated indefinitely in all directions so that each ice crystal or sample of water is traversed by a continuous tridimensional network. Every hydrogen nucleus tends to lie on a line connecting two oxygen nuclei 2.76 A. apart. It is 0.99 A. distant from the nucleus of its own oxygen atom as already noted, and 1.77 A. from the nucleus of the oxygen in its nearest neighbor. The proton is said to form a hydrogen bond or bridge between the two oxygens. These bonds are quite strong, requiring energy of 4500 small calories to break 6×10^{23} bonds. Hydrogen bonding of two oxygen atoms explains also the stability of double molecules such as the dimer of formic acid



and structures of minerals such as dispore $AlHO_2$ (not to be written Al_2O_3-H_2O). Hydrogen bonds between two fluoride ions explain the

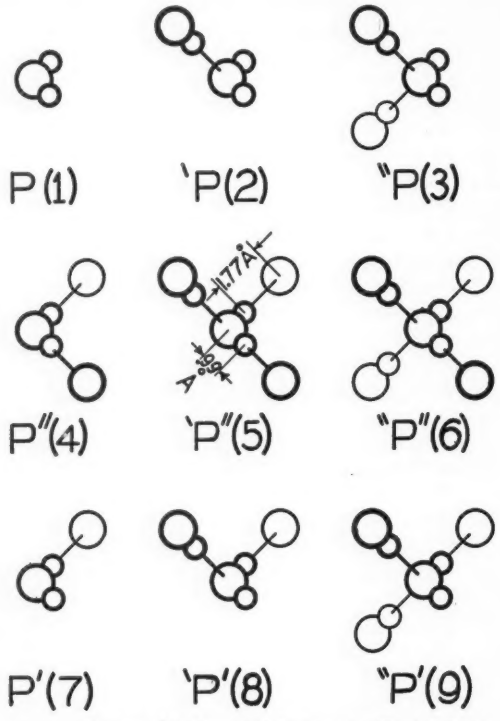


stability of the acid fluoride ion HF_2', inexplicable in terms of classical theory, since a hydrogen nucleus cannot possibly hold two electron pairs. Hydrogen bonds between nitrogen atoms and oxygen atoms unite chains of amino acids to form highly complex protein molecules and so on.

Bernal and Fowler,[5] pioneers in the X-ray examination of ice, thought that the fourfold coördination of water molecules afforded a perfectly orderly pattern running through the entire ice crystal and similar to that found in quartz. But later X-ray data showed that the arrangement was not quite so orderly, and Pauling

[3] MECKE, *Z.Physik*, **81**, 313 (1933).
[4] PAULING, "The nature of the chemical bond," 1st ed., Cornell University Press, Ithaca, N. Y., **1939**, p. 71.
[5] BERNAL AND FOWLER, *J. Chem. Phys.*, **1**, 515 (1933).
[6] KATZOFF, *ibid.*, **2**, 841 (1934).
[7] MORGAN AND WARREN, *ibid.*, **6**, 666 (1938).

actually calculated the degree of randomness from the thermal properties of ice at low temperatures. Cross, Burnham, and Leighton[8] analyzed the Raman spectrum of ice and of water, and showed how the OH oscillators were perturbed by hydrogen bonding to hydrogen and oxygen atoms in other water molecules. They decided that at −183°C. the fourfold coördination of ice is almost complete. In ice near the melting point, four-coördination greatly predominates, but appreciable amounts of three- and two-coördinated molecules were found (see Figure 3). In this temperature in-



Courtesy of the Journal of the American Chemical Society

FIGURE 3.—TYPES OF COÖRDINATION OF WATER

terval, then, some hydrogen bonds have been broken, and the molecular pattern has become somewhat irregular. At 0°C., about 15 per cent of the hydrogen bonds still present break all at once, so that there is a nine per cent shrinkage when ice turns to water. From 0° to 4°C. the further shrinkage due to breaking of hydrogen bonds more than compensates for the expansion due to increasing thermal motion, but above 4°C. the latter effect barely predominates, and water has a positive coefficient of thermal expansion, although this is still much smaller than that of a typical liquid such as carbon tetrachloride. The liquid range of water, 100° at one atmosphere, is unexpectedly long due to the persistence of hydrogen bonds. At 100° all the remaining hydrogen bonds are broken, so that the heat of vaporization of water is abnormally high, 9720 cal./mol. Unlike hydrogen fluoride, water forms no hydrogen bonds in the vapor phase, which contains single molecules almost exclusively.

The surface tension of water at 20°C. is 72.75 dynes/cm. as against 26.77 for carbon tetrachloride and 28.88 for benzene, again pointing to the cohesive effect of hydrogen bonds.

If water is introduced between the oppositely charged plates of a condenser, the negative ends of the water dipoles will be attracted toward the positively charged plate and lower the surface density of its positive charge. Similarly, the positive ends of the water dipoles will lower the surface density of negative charge at the opposite plate. As a result, the electric field at any point between the plates is greatly weakened. In other words, we say that water has an abnormally high dielectric constant, namely 80. If the dipole orientations could be eliminated, water would have a dielectric constant of 1.77 only. At very small distances from a charged ion in water, not exceeding 2 A., *i. e.*, 2×10^{-8} cm., the dielectric constant is about 3.

Evidently the properties of ice and water become logical when explained in terms of small dipoles with a strong tendency toward tetrahedral coördination. The same is true of ionic compounds in water solution and of hydrated crystals.

HYDRATION OF IONS IN SOLUTION

Cations in water solution tend to attract the negative or oxygen ends of nearby water dipoles. A simple anion attracts one of the water protons, so that the line connecting the nuclei of the anion and of the water oxygen passes through that proton. The number of water molecules which could actually touch a given ion all at once depends upon geometrical considerations. The bigger the ion, the greater the number of water molecules that could touch it all at once. Consider now the cations of the alkali metals. Water molecules can approach much more closely the unbalanced positive charge on the nucleus of the lithium ion than that of the much larger cesium ion. As a result, the lithium ion in spite of its small radius is much more strongly hydrated, and attains in consequence a total radius greater than that of cesium ion. At 18°C., the ionic conductances of lithium and cesium ions are 99.0 and 135.0 reciprocal ohms. There is much evidence that the big ions such as Cs^+ and I^- do not restrict either the motion or the orientation of water molecules very much, although I^- is rather the more efficient of the two. In the series of ten-electron ions Na^+, Mg^{+2}, Al^{+3}, the attraction for water molecules increases rapidly from Na^+ to Al^{+3}. The increasing magnitude of unbalanced nuclear charge progressively condenses the electron cloud, so that the radii of the three cations are 0.95, 0.65, and 0.50 A., respectively. Roughly speaking, Al^{+3} as compared with Na^+ has three times the charge at half the distance from the nucleus. The proton, because of its excessively small size, can make

[8] CROSS, BURNHAM, AND LEIGHTON, *J. Am. Chem. Soc.*, **59**, 1134 (1937).

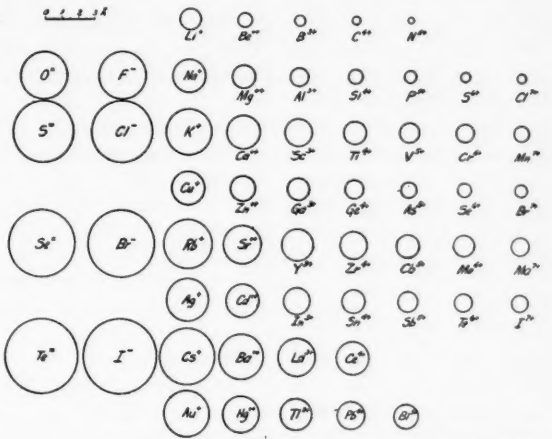
contact with one or two water molecules but no more. Additional water molecules will show decreasing orientation and restriction of motion as the distance from the proton increases. The formula of the so-called oxonium ion OH_3^+ is thus preferable to the formula H^+ which denotes an unattached proton. But neither formula is wholly adequate. The familiar experiment of heating blue vitriol crystals and then pouring water on the white product convinces every student that copper sulfate solution owes its blue color to hydrated copper ions. This at once suggests that many other ions are strongly hydrated, even though symbols such as Cu^{+2}, Zn^{+2}, Fe^{+2} are still used in writing equations. Now when ammonia is added to copper sulfate solution the appearance of the purple color should be pictured as the result of a competition between ammonia and water molecules for cupric ions in which the ammonia molecules, though fewer in number, displace the water molecules almost completely.

$$Cu(OH_2)_x^{+2} + 4NH_3 \rightarrow Cu(NH_3)_4^{+2} + xH_2O$$

A further consequence of hydration is noted in studying the volume changes which occur when salts are dissolved in water. If you dissolve 260 grams of cesium iodide—one formula weight—in a large volume of water at 0°C., the volume of the solution exceeds the volume of the water by 57 cc. But if you repeat the experiment with one mol of sodium fluoride, the volume of the solution is 2.8 cc. smaller than the volume of the water alone. In other words, the strong attraction of the small ions for water dipoles partially breaks down the open network of water molecules, so that the solution approaches more nearly the close-packed arrangement. The volume changes are nearly the same in deuterium water as in ordinary water.

Starting with a cation of given radius, the number of spheres which can touch it simultaneously is governed by the *radius ratio*. Thus if a tetrahedron of water molecules or of anions is to touch the cation, the radius ratio r_c/r_w or r_c/r_a must be at least 0.225. If six spheres are to touch the cation in octahedral coördination this ratio must be as large as 0.414. For eight spheres in cubical coördination the radius ratio must be at least 0.713. For twelve spheres coördinated as a cubo-octahedron it must be at least unity. These figures can be lowered a little in practice because it is not always necessary, for the stability of the structure, that the central sphere touch all the coördinated spheres at once. None the less, these ranges for the radius ratio make possible some valid predictions.

First, you can represent an oxygen acid as the addition product of one or more water molecules to one of acid anhydride. Assume that the anion of the oxygen acid contains a cation coördinating oxide ions of radius 1.35 A. Of course this is a crude picture, because the electron clouds of the oxide ions tend to shift toward the central cation. Thus the oxide ions shrink and the central cation is inflated. The radii found in the literature (see Figure 4)[9] are based on ions which have attained some such adjustment. Now the radii of B, C, and N ions are less than 0.225 times the radius of the oxide ion, so that tetrahedral coördination is unstable, so we find the ions[10] BO_3^{-3}, CO_3^{-2}, NO_3^-. The radii



From "The Nature of the Chemical Bond," by Linus Pauling
Cornell University Press

FIGURE 4.—CRYSTAL RADII OF IONS

of Si^{+4}, P^{+5}, S^{+6}, Cl^{+7}, As^{+5}, Se^{+6} all lie between 0.225 and 0.414 times the radius of the oxygen ion, so we observe SiO_4^{-4}, PO_4^{-3}, SO_4^{-2}, ClO_4^-, AsO_4^{-3}, SeO_4^{-2}, all tetrahedral ions. The ions $[Sn(OH)_6]^{-2}$, $[Sb(OH)_6]^-$, and $[TeO_6]^{-6}$ all have radius ratios between 0.414 and 0.713. But now the fluoride ion is slightly smaller than the oxide ion, so that the coördination number for fluoride may exceed that for oxide ion. Thus we have AlF_6^{-3} instead of AlO_4^{-5}; PF_6^- instead of PO_4^{-3}; SF_6 instead of SO_4^{-2} and even $[SnF_8]^{-4}$ instead of $[Sn(OH)_6]^{-2}$.

The small water dipoles play a unique role in the formation and stability of many ionic crystals. Anions in general are larger than the common bivalent or tervalent cations because their extra electron or electrons distend their outer shells. When the anhydrous salts of such small cations are cc red, it is impossible to have ionic crystals like so um chloride where each sodium is in contact with an octahedron of chloride ions and vice versa. For instance, the radius of aluminum ion is 0.57 A., and that of chloride ion 1.81; the radius ratio is only 0.32, so that tetrahedral coördination is the highest to be expected. As this will not provide for all the chloride ions, the crystals of anhydrous aluminum chloride are found to be made up of layers of chloride ions all in contact, between which layers of aluminum ions rattle around at regular intervals. But if you crystallize the same salt from water, each aluminum ion surrounds itself with an octahedron of six water molecules. The radius of the aquo ion $Al(OH_2)_6^{+3}$ is 3.3 A., so that it readily makes contact with even

[9] PAULING, *op. cit.*, p. 348.

[10] PAULING, *J. Am. Chem. Soc.*, **55**, 1895 (1933).

twelve chloride ions. Each of the six water molecules is hydrogen bonded to two chloride ions so that a stable lattice easily results.

The beryllium ion is very small (r = 0.31 A.) and could scarcely form even a tetrahedron with the big SO_4^{-2} ions (r = 1.5 A.) But when a tetrahedron of water molecules is added, the aquo ions $Be(OH_2)_4^{+2}$ pack readily with tetrahedral sulfate ions to form $Be(OH_2)_4^{+2}SO_4^{-2}$. When these crystals are formulated as $BeSO_4 \cdot 4H_2O$, the dot represents ignorance of the true position of the water molecules.

Nickel sulfate forms a hexahydrate in which six water molecules form an octahedron around each nickel ion. These octahedra are packed together with sulfate tetrahedra. Below 54°, a seventh water molecule can find lodgment, not making contact with the nickel ion, but bound tetrahedrally by hydrogen bonds to one sulfate oxygen and to three of the six octahedral water molecules.[11] All this comes about without any important modification of the hexahydrate structure.

In copper sulfate pentahydrate, each cupric ion is octahedrally coördinated. The six groups include four water molecules and two oxygen ions belonging to sulfate groups. The fifth water molecule does not touch any cupric ion, but is tied by hydrogen bonds to *two* tetrahedral waters and to *two* sulfate oxygens.

In gypsum, $CaSO_4 \cdot 2H_2O$, the calcium and sulfate ions are bonded to form plane layers one ion deep. These alternate with double sheets of water molecules. Each water molecule is bonded to one calcium ion and to one sulfate ion in one layer and to one sulfate ion in the other layer. It is not surprising that cleavage planes easily develop between the layers of calcium and sulfate ions.

Sodium sulfate decahydrate crystals resemble ice, in which sodium ions and sulfate ions are so widely dispersed that they are not bonded to each other. Above 32.38° the whole lattice collapses, and the anhydrous sodium sulfate forms a supersaturated solution in its own crystal water.

Most crystals, indeed, collapse when even a part of their crystal water is driven off, but a group of minerals known as zeolites are exceptions to this rule. For instance, sodalite, $Na_4Al_3Si_3O_{12}Cl$, is made up of a very stable tridimensional network of SiO_4 tetrahedra and AlO_4 tetrahedra. This network is so open that it can accommodate not only the sodium and chlorine atoms, but a large number of water molecules as well. This so-called zeolite water can be expelled without ruining the crystal, and reintroduced without disturbing the anhydrous product. It is even possible to substitute, for water, other volatile substances such as ammonia, alcohol, or mercury. The low heat of evaporation of zeolite water shows that its molecules are merely adsorbed upon the crystal network and are not part of a bonded structure.

[11] See EVANS, "An introduction to crystal chemistry," Cambridge University Press, Cambridge, England, 1939, Fig. 67, p. 277.

If now we turn back from the salts of bi- and tervalent cations to those of the alkali metals, we discover few hydrated salts after passing through lithium and sodium and reaching potassium, rubidium, and cesium. These last three cations, owing to their small valence and large radii, attract water dipoles feebly. On the other hand, their large radii allow octahedral or cubical coördination even with large anions so that coördination of water molecules is no longer a prerequisite for formation of these very stable ionic crystal types.

The heats of solution of ions in water have very important consequences. If you transfer a pair of ions from vacuum to a given medium, the energy evolved

$$E = \frac{e^2}{2r}\left(1 - \frac{1}{D}\right)$$

ergs where e is the electronic charge, D the dielectric constant, and r the radius of the ion in centimeters. If the medium is water, for which D = 80 the expression becomes $e^2/2r$ ergs very nearly. This energy is the most important part of the heats of solution of ions, L. The heat evolution per gram ion dissolved is 126,000 calories for chloride ion; 92,000 calories for sodium ion; 446,000 calories for magnesium ion, and 1,070,000 calories for aluminum ion. Of course these figures include the energy changes due to secondary effects.

The very existence of separate sodium and chloride in water depends on these heats of solution. You will remember that the opponents of Arrhenius, about 1890, said that it was absurd to speak of sodium and chlorine atoms separately stable in water. Now suppose that you could remove 58.5 grams of sodium chloride from water and disperse it as separate ions in a vacuum. To your surprise you would find that electrons would tend to migrate from chloride ions to sodium ions, so that the gas would tend to be converted into dispersed sodium and chlorine atoms with evolution of 31,000 calories. Indeed, no alkali halide except cesium fluoride is stable as highly dispersed ions in the gaseous state. Now retrace your steps by converting the atoms, on paper at least, to ions, and then dissolve them in much water evolving the sum of 91,000 and 92,000 calories. The net evolution of heat, ending with dissolved sodium and chloride ions, would be 152,000 calories. From experience we could be quite sure that a process so highly exothermic will be complete at room temperature. Sodium chloride ionized in water owes its stability to the heats of solution of its ions and the same is true of all the alkali halides, cesium fluoride alone excepted.

You could arrive at the same conclusion through a more detailed argument. It is not hard to prove that the energy expended in removing the valence electrons from 23.0 g. of sodium atoms dispersed in a vacuum is 118,000 calories, but only 27,000 calories in water. The difference is 91,000 calories, the heat of solution of sodium ion. If you add these electrons to 35.5 g. of chlorine atoms dispersed in a vacuum you evolve 87,000 calories, but if you do it in water you evolve 87,000 + 92,000, that is, 179,000 calories. The alge-

braic sum of $-27{,}000 + 179{,}000$ is 152,000 calories as before, the energy evolved in converting the dispersed atoms into ions in water. The same argument applies to any pair of ions.

This one example suggests how greatly oxidation-reduction potentials in water involving ions are affected by heats of solution of the ions. The same is true of the course of oxidation-reduction reactions.

The solution of ionic crystals in water could not occur appreciably except for the heats of solution of the ions. A sodium chloride crystal is a lattice of discrete sodium and chloride ions held very firmly together by mutual electrostatic attractions. To convert 58.5 grams of sodium chloride crystals to ions dispersed in a vacuum requires energy expenditure of 184,000 calories,the *lattice energy* of sodium chloride. If next you dissolve these dispersed ions in water, 183,000 calories will be evolved. The molar heat of solution of sodium chloride *crystals* in water is therefore endothermic to the extent of 1000 calories. The process is spontaneous in spite of the necessity for heat absorption because the disorder of the system is increased when you pass from the highly ordered crystals to the disordered state of the solution. Everybody knows how much energy is needed to bring order out of chaos in the affairs of everyday life. It is not surprising, then, that the production of increased disorder should assist the solution process to occur even if heat has to be withdrawn from the surroundings at the same time. In the language of thermodynamics, the outcome is due to the increase in the entropy of the system.

Suppose, however, that we had worked out silver chloride instead of sodium chloride. We could first expend the lattice energy of silver chloride, 214,000 calories, and convert 143.5 grams of crystals into dispersed gaseous ions. The ions are then dissolved in water, evolving $(106{,}000 + 92{,}000)$, that is, 198,000 calories. The urge toward greater disorder, which is nearly the same as for sodium chloride, is insufficient to force the absorption of 16,000 calories from the surroundings, so that silver chloride cannot dissolve appreciably. Professor O. K. Rice, in his admirable book "Electronic Structure and Chemical Binding,"[12] shows how to predict quantitatively such solubilities from the heats of solution, the lattice energies, and the changes in degree of order which occur.

Silver iodide is even more interesting than silver chloride. If you disperse silver ions and iodide ions in a vacuum, electrons would tend to migrate from iodide ions to silver ions to form the corresponding atoms with evolution of 99,400 cal./mol. But since the lattice energy of silver iodide is 208,200 calories, these crystals will still form readily from either the dispersed ions or the dispersed atoms. But there are two other paths which the dispersed ions could take. They could dissolve directly in water, *or* after turning to dispersed atoms, they could condense to solid silver and solid iodine. You might ask whether the salt dissolved in water would tend to pass into solid silver and solid iodine. This reaction can easily be made to occur indirectly in concentrated solutions by a very simple experiment. Set a beaker of molar silver nitrate beside a beaker of molar potassium iodide, and connect the two with a lampwick soaked with saturated potassium nitrate solution. Insert a platinum electrode in each solution and short-circuit the electrodes. Silver crystals will soon appear on the one electrode and a brown solution of iodine in iodide solution around the other. Now connect the electrodes to a millivoltmeter, and the cell will show an E.M.F. of 0.26 volt. This means that silver ions in molar concentration can attract electrons through the wire away from iodide ions in molar concentration in presence of iodine with an energy evolution of 6000 cal./mol. Now pour out the molar solutions and substitute 0.006 molar solutions, not forgetting to add iodine to the dilute iodide solution. The cell will show no further reactions, and its E.M.F. will be zero, which means that the 0.006 molar solutions have the same oxidation-reduction potential against silver and iodine respectively. The increased disorder of the two 0.006 M solutions due to the increased number of water molecules has lowered their potential energies in contrast to the molar solutions. The increase in stability is 0.26 electron volt or 6000 calories. The 0.006 M solutions, however, are still unstable with respect to silver iodide crystals, since a single solution 0.006 M in Ag^+ and in I^- will readily precipitate this solid. A saturated solution of silver iodide in water is only 10^{-8} molar, a solution with potential energy 16,000 cal. less than that of the 0.006 M solutions. So it is no wonder that solid silver iodide added to water does not become converted into silver and iodine, as it *would* if its solubility exeeded 0.006 mol/liter.

The same method of reasoning from data which serves to predict the solubilities of salts will also predict the strength, or weakness, of given acids in water solution. Instead of undertaking to form aqueous ions, starting with a mol of NaCl crystals, let us start with 36.5 grams of gaseous hydrogen chloride. To convert this into gaseous ions dispersed in a vacuum would require expenditure of 319,000 calories. But the solution of these gaseous ions in water will evolve 343,000 calories. The highly exothermic character of the combined reactions (24,000 calories) makes it safe to predict that the formation of hydrated hydrogen and chloride ions will be virtually complete.

If a similar calculation for another gaseous acid, such as hydrogen sulfide, indicated a highly endothermic overall process, we could predict that the acid would be feebly ionized in water. In the majority of acids the necessary data on gaseous ions are not available. Many attempts have been made to predict the strength of acids from other data. Of these, the treatment of weak oxygen acids by Kossiakoff and Harker[13] was especially successful. Their arguments are simplified in O. K. Rice's book, already mentioned.[12] Take the

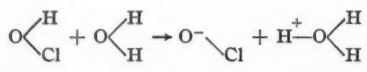
[12] RICE, "Electronic structure and chemical binding," McGraw-Hill Book Co., Inc., New York City, 1940, 511 pp.

[13] KOSSIAKOFF AND HARKER, *J. Am. Chem. Soc.*, 60, 2047 (1938).

weak hypochlorous acid as an example. The ionization proceeds by transfer of protons to water molecules to form oxonium ions.

$$ClOH + OH_2 \rightleftarrows ClO^- + OH_3^+$$

The transfer can be represented diagramatically as follows:



followed by the exchange of the proton with other water molecules. In this case it turns out that the proton must be moved 0.80 A. from its first position to its second position adjacent to the water molecule through a medium of dielectric constant of 3 (not 80, since it remains well within a distance of 2.0 A. from the charged particle). The electrical work expended in moving the proton 0.80 A. from the acid to the water molecule is 52,400 cal./mol. But now it has fifty-five possible partners for each single partner before, since in molar hypochlorous acid the ratio of water to acid molecules is 55. The resultant increase in disorder lowers the necessary electrical work by 2400 calories. The increase in hydration inevitable when a water molecule is turned into an oxonium ion would contribute 50,000 calories more, except that this contribution is offset to the extent of 7000 calories by the striking decrease in the disorder of water molecules attendant upon formation of oxonium ion. Combining these four quantities with due regard for sign, the necessary work to be done on the system becomes 10,230 calories. Thereupon the ionization constant K of the hypochlorous acid results from the indispensable thermodynamical equation

$$-RT \times 2.3 \log K = 10{,}230$$

where R is the gas constant, 1.985 calories per mol per degree, T the absolute temperature, and 2.3 the factor necessary to convert natural to common logarithms. From this equation K comes out 1.6×10^{-8} as compared with a measured value of 6.4×10^{-7}, which is not a bad agreement. The agreement between log K as calculated and as found for 26 other oxygen acids is in general about as good as for hypochlorous acid.

This brief discussion of water suggests possibilities for interpretation of the properties and behavior of other substances. Most students prefer the study of organic and physical chemistry to that of inorganic because the facts of inorganic chemistry appear unrelated. This impression should not be allowed to persist. The teaching of inorganic chemistry will gain in vitality and coherence if frequent glimpses are given of the general principles which unify the entire subject.

WILHELM BÖTTGER

(Frontispiece)

ANALYTICAL chemistry is the indispensable foundation of the other branches of the science; but precisely because it has been such a good servant, it has undeservedly acquired, in some chemical circles, a reputation of inferiority. Its importance was paramount during the development of scientific chemistry, and the greatest minds of that time devoted a considerable portion of their efforts and talents to the advancement of this branch. However, when chemistry began to subdivide, the analytical field suffered a partial eclipse and its development was seriously arrested. This condition was not due solely to the fact that it could not offer attractions comparable to those held out by organic synthesis, for example, but rather because analytical chemistry was suffering from a serious internal infirmity. No matter how numerous or complete the details, their sum could never equal the insight required for a knowledge of the whole, so long as general points of view were not available. Analytical chemistry was taught as an art, its practioners were little more than skilled craftsmen, and no significant progress was possible as long as there was no underlying body of theory. Besides the more or less empirical modification of existing recipes and the haphazard discovery of new reactions and reagents, the field seemed to be fairly well exhausted.

The development of physical chemistry changed this picture. It provided the essential foundation for a renaissance of analytical chemistry. The "Exodus" of this revival was Ostwald's, "The Scientific Foundations of Analytical Chemistry" (1st ed., 1894). Wilhelm Böttger was trained and spent his entire teaching career in Ostwald's famous Physikalisch-chemisches Institut of the University of Leipzig. Therefore, it is not at all strange that he is one of that comparatively small number of contemporary chemists who have devoted their professional lives to the advancement of analytical chemistry, particularly through the application of physico-chemical principles.

Wilhelm Böttger, born at Leisnig (Saxony) on October 21, 1871, entered chemistry after completing the standard pharmaceutical curriculum. At the suggestion of Th. Paul he chose as the subject for his doctorate research "The electrometer as indicator in the titration of acids and bases," a selection which foreshadowed his future major interest. After a year as assistant to Wallach at Göttingen, and a similar period under Ostwald, he was in Leipzig in 1903 as *privatdozent* for analytical and physical chemistry. In October, 1904, he came to America as Research Associate at Massachusetts Institute of Technology. His impressions of the American colleges, recorded in his "Amerikanisches Hochschulwesen" (1906), are still excellent reading. He returned to Ostwald's Institute in 1905, received the Ph.D. degree in 1907, and remained there without break for more than thirty years, refusing offers of other posts. He passed through all the academic grades and was made emeritus in 1937 when he reached the retiring age.

As might be anticipated from his training and environment, Professor Böttger and his students have worked chiefly on the application of physical chemical methods to analytical problems. The main studies have dealt with: sensitivity of chemical reactions; refinement of quantitative electroanalytical procedures; microchemical methods; amphoteric hydroxides; elimination of indicator errors in visual titrations; etc.

Of no less importance are his literary activities. His "Qualitative Analyse" (1st ed., 1902) was the first text in which qualitative analysis was treated entirely on the basis of the Arrhenius theory. It has gone through seven editions and has been translated into Russian, Italian, and English. He collaborated in such important undertakings as: Landolt-Börnstein; Lunge-Berl; "Handwörterbuch der Naturwissenschaften." Since 1931 he has edited the extremely valuable series "Die chemische Analyse." He is editor of the important "Physikalische Methoden der analytischen Chemie," and himself wrote the sections on electroanalysis (1160 pages) and potentiometric analysis (282 pages).

This latter contribution exhibits particularly well the character of his scientific work, which has been largely devoted to the reconciliation of "theory" and "practice."

—Contributed by Ralph E. Oesper, University of Cincinnati

The Qualitative Chemical Identification of the Natural Sugars

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IN EFFECTING isolations from natural sources sugars are often encountered; and unless one is a specialist in the field of carbohydrates, the identification of an unknown sugar is likely to occasion considerable difficulty. Although a host of characterizing reactions and tests have been developed for the various sugars, no systematic scheme of identification such as exists in organic chemistry has as yet been put forward. The following scheme has been in use in our laboratory and has proved very valuable for a quick identification of carbohydrates with a minimum of effort. It covers most of the natural sugars and includes the polysaccharides most frequently encountered. The rarer sugars not available have been omitted, but they can be fitted into the proper groups by the individual investigator. Mention of these is made in the explanations of the test reactions. No confirmatory tests or derivatives have been listed, since these may be obtained from a number of good references (*1*, *2*).

Many students inexperienced in sugar chemistry have made use of the scheme and have arrived at correct conclusions.

DISCUSSION OF THE TEST REACTIONS

The reactions used in the scheme are standard tests and many of them may be found in several recent laboratory manuals. The results obtained with them, however, are often dependent upon the conditions used, and unless these are observed erroneous conclusions may result. A discussion of the tests follows, arranged in alphabetical order according to the name of each test.

Aniline Test.—This test (*3*) is most effective for distinguishing pentoses from uronic acids. One mg. of sugar is dissolved in two cc. of water, two cc. of glacial acetic acid and five drops of pure aniline are added. The solution is heated just to boiling and allowed to stand. Pentoses give a bright red color, uronic acids and pentosans do not.

Barfoed's Test.—Barfoed's reagent (*4*) serves very well for the quick differentiation between reducing mono- and disaccharides. One mg. of the sugar is dissolved in 2.5 cc. of the reagent, and the tube is placed in a boiling water bath. The time at which the first perceptible reduction occurs is then noted. Monosaccharides reduce within three minutes, whereas disaccharides generally require twenty minutes. Melibiose, however, reduces in five minutes. For comparison, it is advisable to run known sugars at all times in using this reaction.

If there is any doubt concerning the differentiation between mono- and disaccharides the Willstätter-Schudel titration should be resorted to (*5*).

Sucrose may also be differentiated from melezitose by means of Barfoed's reagent. Twenty-five mg. of the unknown sugar are dissolved in 2.5 cc. of the reagent and placed in a boiling water bath. Sucrose will reduce in ten minutes, whereas melezitose requires fifty minutes.

Sodium chloride as an impurity should be avoided in the use of this test, since it interferes with the reaction.

Benedict's Test.—This is the well-known qualitative reagent of Benedict (*6*) and hardly needs any elaboration. Fehling's solution will work just as well, but Benedict's is preferred, because it is less likely to give reduction with non-sugar impurities. A sample of several milligrams is introduced directly into 2.5 cc. of the test solution and treated in the usual manner.

Benzhydrazide Test.—Benzhydrazide can be prepared easily from benzamide and hydrazine hydrate (*7*). It forms a clearly defined derivative with *l*-arabinose which serves to differentiate it from *d*-xylose and *d*-ribose.

One hundred thirty mg. of *l*-arabinose are dissolved in 0.25 cc. of water and 4.8 cc. of absolute alcohol are added. The solution should remain clear. One-half mg. of benzhydrazide is added and the whole is refluxed for thirty minutes. Upon standing for ten to fifteen hours the *l*-arabinose benzhydrazone crystallizes out in beautiful clusters. With *d*-xylose and *d*-ribose no insoluble benzhydrazone will appear. After recrystallization from alcohol the benzhydrazone melts at 210°–212°.

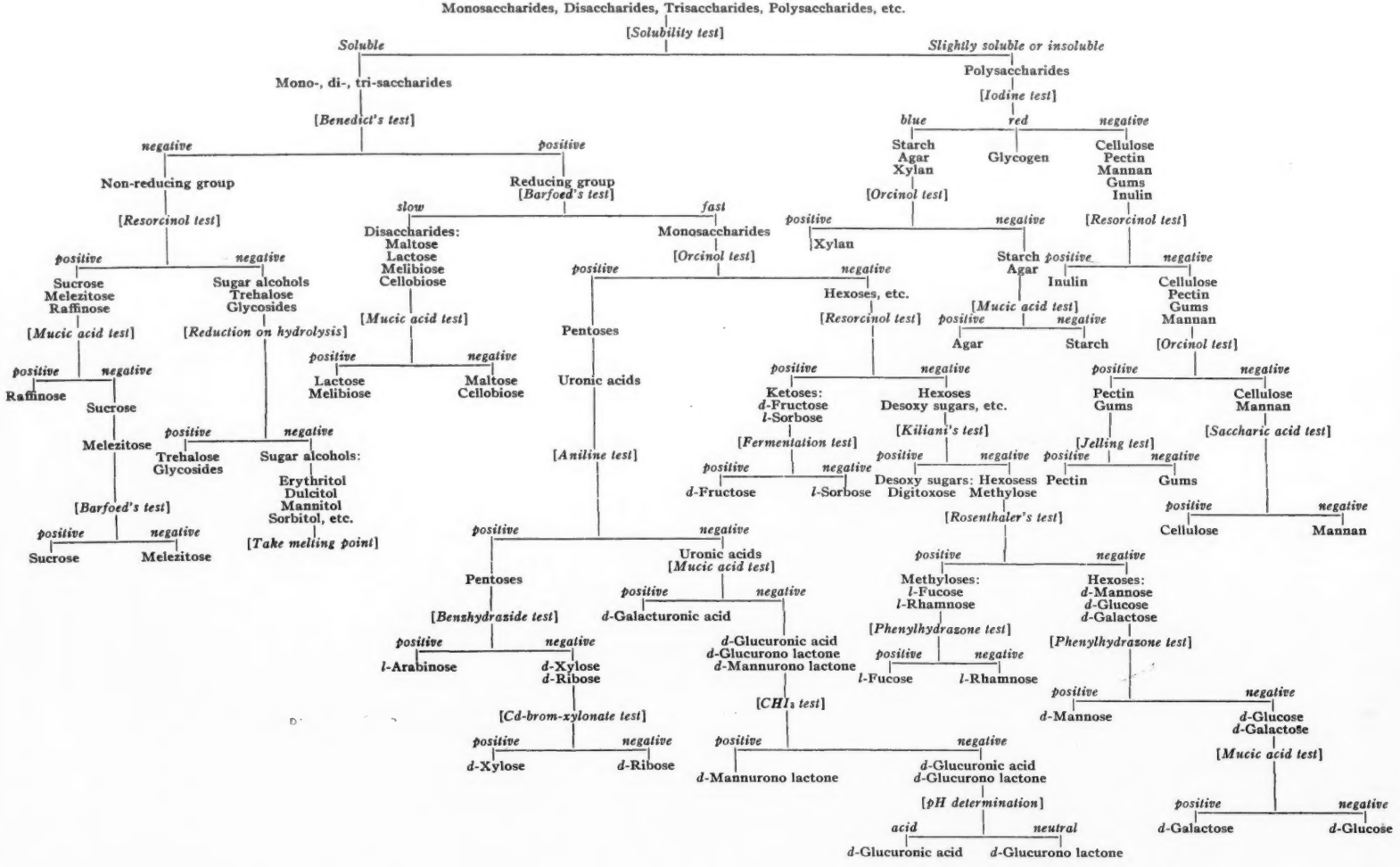
Cadmium-brom Xylonate Test (Bertrand's Reaction).—At least 100 mg. of sugar must be used in this test to give the characteristic crystals of the cadmium bromide double salt. The following procedure has been found to be most satisfactory.

One hundred mg. of sugar is placed in a test tube with one cc. of water and 0.5 g. of cadmium carbonate. Eight drops of bromine are added and the mixture is warmed in a water bath at 50° for half an hour. After the reaction mixture has stood for some hours several cc. of water are added, and the solution is filtered to remove the cadmium carbonate. The filtrate is concentrated to one cc. in a vacuum desiccator and one cc. of alcohol is added. Crystallization takes place within a short time. The crystals should be filtered off and recrystallized by dissolving in one cc. of water and adding one cc. of alcohol. Under the microscope the crystals appear boat-shaped (*8*).

This test can be run on a micro scale by reducing the volumes and weights to one-tenth of those indicated.

Fermentation Test.—A one per cent sugar solution is

OUTLINE OF THE QUALITATIVE ANALYSIS OF THE SUGARS



triturated with a small piece of baker's yeast. A small test tube is filled with the suspension and inverted in the container so that no air is admitted into the tube. Fermentation will be evidenced in a few hours by the production of gas in the tube.

Iodine Test.—A number of natural polysaccharides give color tests with a dilute solution of iodine in aqueous potassium iodide. The intense blue color with starch is the most characteristic. Glycogen will give a wine-red color if pure. Agar and xylan do not dissolve to give the test in solution under the conditions, but the suspended particles adsorb iodine strongly to give blue to purple colors.

Iodoform Test.—The usual alkaline hypoiodite conditions prevail in this test. *d*-Mannurono lactone breaks down in alkaline solution to yield a decomposition product capable of producing iodoform. *d*-Mannosaccharic acid lactone also does this, but the free acids in both cases do not. Mannuronic acid is invariably isolated as the lactone; the free acid can be obtained only under special conditions.

Jelling Test.—The differentiation between gums and pectin is usually quite easy. Gums are often soluble in cold water and are the only polysaccharides that give a clear solution. Pectin is somewhat soluble in warm water, more so if a few drops of dilute acid are added. A solution thus obtained will gel immediately upon the addition of an equal volume of alcohol. A solution of a gum requires considerable alcohol before the gum is precipitated out as an amorphous powder.

Kiliani's Test for Desoxy Sugars (*9*).—A one-mg. sample of sugar is dissolved in 4.5 cc. of acetic acid containing some iron in solution and mixed slowly with 4–5 drops of sulfuric acid containing some iron in solution. An indigo-blue color is developed in the presence of desoxy sugars.

Iron-containing acetic acid is made up by adding one cc. of five per cent aqueous ferric sulfate to 100 cc. of glacial acetic acid. The sulfuric acid reagent is also made by adding one cc. of five per cent aqueous ferric sulfate to 100 cc. of acid.

Mucic Acid Test.—One hundred mg. of sugar are dissolved in two cc. of water and one cc. of concentrated nitric acid is added. The solution is heated in a test tube in a boiling water bath for one and one-half hours, cooled, and allowed to stand 12–15 hours. Mucic acid will crystallize as fine white rectangular slivers (*10*). The microscopic examination of mucic acid should always be accompanied by a determination of the melting point (212°–215°).

In the case of galacturonic acid, bromine can be substituted for nitric acid as the oxidizing agent, but this is not necessary. With raffinose the crystallization of the mucic acid may be delayed somewhat; it may be hastened by increasing the quantity of sugar and by seeding with a minute quantity of mucic acid.

Orcinol Test (*Bial's Test*).—The orcinol reagent (*11*) will give a characteristic color with pentoses, uronic acids, and any molecule containing them as an integral part. The usual interpretation of the results, however, needs modification as follows. The only indication that should be interpreted as positive is the production of a blue color or of a dark blue precipitate. This blue color and precipitate are produced by furfural. If there is any question about the color the addition of *n*-butyl alcohol will cause the precipitate to go into solution, after which the blue color is clearly distinguishable. Digitoxose is reported to give a positive test with the orcinol reagent. It, however, gives a green precipitate which upon solution with butyl alcohol does not show up as the typical blue of the furfural color. The dark brown color which methyl pentoses yield has also been misinterpreted by some as a positive orcinol test. The test is very sensitive for all furfural producers. One mg. of substance per three cc. of the reagent is quite sufficient to produce a color and precipitate upon warming in a boiling water bath for a few minutes.

Pectin is slower in the orcinol test than gums and requires somewhat more material. Due also to decomposition products the final solution upon dilution with *n*-butyl alcohol has a greenish cast to it instead of a clear blue.

Phenylhydrazone Test.—*d*-Mannose and *l*-fucose form insoluble phenylhydrazones which are very suitable for the characterization of these two sugars.

For *d*-mannose the following proportions are suitable. Twenty-five mg. of sugar, 0.3 g. phenylhydrazine hydrochloride, and 0.2 g. of anhydrous sodium acetate are dissolved in three cc. of water and allowed to stand. In a few minutes the grayish white phenylhydrazone of mannose will start to separate. It may be filtered off and recrystallized from water, melting point 188°.

The following proportions are best suited to *l*-fucose. One hundred mg. of sugar, 0.3 g. of phenylhydrazine hydrochloride, and 0.2 g. of anhydrous sodium acetate are dissolved in three cc. of water. Upon scratching the sides of the container the white fucose phenylhydrazone will precipitate in a few minutes. After recrystallization from a small quantity of water the melting point is 170°. The proportions of 50 mg. of *l*-fucose, 44 mg. of phenylhydrazine hydrochloride, 30 mg. of sodium acetate dissolved in three cc. of water will produce a white phenylhydrazone upon standing for 12–15 hours.

Reduction on Hydrolysis.—Hydrolysis can be effected easily by refluxing a 0.1-g. sample with 25 cc. of 0.6 per cent sulfuric acid for one hour. The solution is then neutralized and a portion of it tested by means of Benedict's reagent.

Sugar alcohols will, of course, show no reduction after hydrolysis, whereas trehalose and the glycosides will. Sugar alcohols, in contrast to most sugars, give good melting points and can be differentiated from each other on this basis (*12*). Those occurring in nature are erythritol, adonitol, *d*-sorbitol, *d*-mannitol, dulcitol, *l*-iditol, perseitol, volemitol, inositol, quercitol, and styracitol. The dibenzal derivatives are conveniently made for confirmation (*13*).

It is beyond the scope of this paper to treat glycosides. The constituent sugars should be obtained from them

by hydrolysis and identified free from the influence of the aglycone.

Resorcinol Test.—The reagent employed in this test is the familiar one developed by Seliwanoff (*14*). Ketone sugars give a red color when heated with the reagent for thirty seconds. The proportion of three mg. of the sugar to three cc. of reagent serves very well. In using this test it is essential that the solution be heated no longer than thirty seconds, since other hexoses will give the test on prolonged heating.

Due to the rapid hydrolysis of fructose glycosides, carbohydrates containing fructose as an integral part of the molecule will give the resorcinol test. Thus inulin, sucrose, and raffinose give the test readily.

Perseulose, tagatose, and glutose have been reported to give this reaction (*15*), but *l*-xyloketose does not (*16*).

Rosenthaler Test for Methyl Pentoses.—Five mg. of the sugar are weighed out and transferred to a test tube, one cc. of acetone added, and three cc. of concentrated hydrochloric acid. The test tube is shaken and placed immediately in a boiling water bath. Methyl pentoses develop a permanent wine-red color, whereas the aldohexoses yield only a light yellow. *l*-Rhamnose gives the test in two minutes; *l*-fucose requires four and one-half to five minutes. If too large a quantity of sugar is used in this test, a brown precipitate is obtained with all sugars.

The ketohexose sugars yield a violet color in the Rosenthaler test which changes to a brown on standing for a short time.

Saccharic Acid Test.—The usual conditions for this test prevail (*17*).

Solubility Test.—Solubility in cold water, although not entirely free from errors, can be used to differentiate between polysaccharides and the mono- and oligosaccharides. A 20-mg. sample of the unknown is shaken with two cc. of cold water. Mono- and oligosaccharides dissolve to form a clear solution and generally solution is rapid. The polysaccharides with a few exceptions dissolve only to a slight extent if at all. Glycogen dissolves readily giving an opalescent solution, but it can be detected quickly by its characteristic color with iodine water. Many plant gums when obtained in powdered form dissolve readily, and, of the polysaccharides tested in this scheme, are the only substances likely to be mistaken for the lower saccharides. They are amorphous, non-reducing, and give the orcinol test for furfural. Perseulose has been reported to be only slightly soluble in water (*18*). It reduces Benedict's solution and gives the resorcin test for ketoses. With the orcinol test it is reported to give a violet color.

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(13) *Ibid.*, p. 23.
(14) See (3), p. 14.
(15) See (1), p. 387.
(16) LASKER AND ENKLEWITZ, *J. Biol. Chem.*, **101,** 289 (1933).
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An Ultramicroscope Cell

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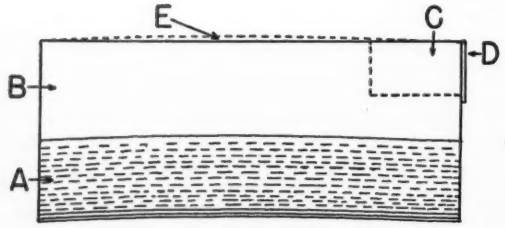

ULTRAMICROSCOPE CELL
A—Webbing
B—Rubber
C—Niche for solution
D—Cover glass
E—Upper surface of rubber leveled off

THE ultramicroscope project described by Miller and Ketterer[1] has been worked out very successfully in this laboratory.

If the glass, hard rubber, or bakelite are not available, the waterproof cell can be cut from a discarded automobile tire, as shown in the illustration. The upper surface is leveled and the 3-mm. niche cut out with a razor blade. It is better to make the cell length about 3 cm. to avoid the lower surface curve of the tire. The other dimensions remain essentially the same. As cover glasses cement well to rubber, the vertical and horizontal openings can be closed securely.

[1] MILLER AND KETTERER, J. CHEM. EDUC., **11,** 570–4 (Oct., 1934).

The Preparation of Ammonium Hydroxide for Laboratory Use

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AMMONIUM hydroxide is used in large quantities for a variety of chemical reactions. The purchase of carboys of the solution is expensive for experiments using large quantities of this reagent. Therefore, an investigation was initiated to determine the best method of preparing this reagent in the laboratory from liquid ammonia. Ammonium hydroxide solution contains approximately seventy per cent of water, the freight on which, together with the heavy carboy and crate, is the largest item of cost. Liquid ammonia in iron cylinders may be purchased in every industrial center.

METHODS OF ABSORPTION

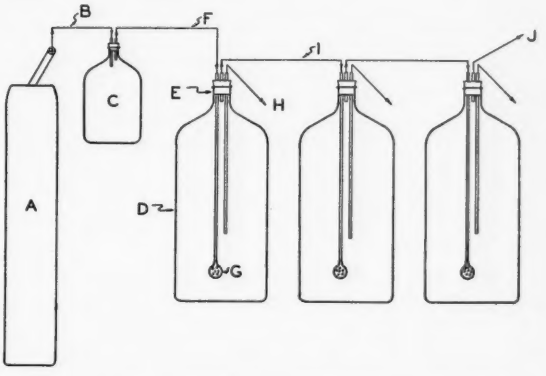
The tower system for absorption of ammonia in a countercurrent flowing stream of water comes to mind first. Several disadvantages are apparent, such as careful control necessary to produce the desired concentration, large capacity, and necessity for removal of heat of solution. In fact, the latter factor is the most important consideration in all systems preparing large quantities of ammonium hydroxide in a short period of time, and cooling must be carried out.

The reaction may be considered according to Le Chatelier's principle

$$NH_3(g) + H_2O\ (1) \rightleftharpoons NH_4OH(Aq.) + \Delta$$

thus the exothermic reaction raises the temperature and shifts the equilibrium to the left, decreasing the concentration of ammonium hydroxide, unless the heat of reaction is removed. Increased pressure is seen to increase the concentrations of ammonium hydroxide obtained.

A simple absorption system utilizing these principles was devised. (See the figure.) Three large carboys were connected in series. A fifty-pound ammonia cylinder (*A*) was connected to the first carboy (*D*) through a one-gallon jug (*C*) which acted as a trap to prevent solution from being sucked into the cylinder. The line *B* was a three-eighths-inch rubber pressure tube, but all lines thereafter (*F*, *I*) were three-eighths-inch glass tubing with rubber tubing at the joints. The carboys were fitted with two-inch rubber stoppers (*E*) in which three holes were cut. One was for the tube *F*, bringing the ammonia into the solution, the second for the tube *I* to pass unabsorbed ammonia into the second carboy, and the third for the three-sixteenth-inch sample tube *H* from which samples of the solution in the carboy could be drawn. In the third carboy the stopper had a small safety tube (*J*) for the passage of unabsorbed gas to the atmosphere. At the end of each inlet tube was a 75-ml. flask (*G*) which had a number of small holes in the body. Because of these holes a large number of small bubbles were formed which increased the gas surface and the rate of absorption. When the ammonia in the cylinder is exhausted, solution will syphon slowly back from the first carboy into the trap (*C*).



In operation, sixty-eight pounds of water are poured into each carboy and the stoppers fastened down with wire or tape. The valve of the ammonia cylinder is opened wide and absorption allowed to continue until the ammonium hydroxide in the first cylinder has reached the desired concentration. The first carboy is then removed and a new one added after the third carboy, the second carboy now being the first carboy. This procedure can be followed until the desired amount of ammonium hydroxide has been prepared. The concentration is determined by titrating the solution with normal acid, or by hydrometer reading of density.

RESULTS

It was found that the first carboy reached the desired normality in about ninety hours. It had a normality of 15.5, the second had reached 8.8, and the third 3.6. The absorption efficiency found by weighing the cylinder and comparing with the carboys was over ninety-five per cent. The maximum concentration obtained was 17 normal. Commercial ammonium hydroxide showed slight variation from 15 normal, and solutions as uniform could be made in this absorption apparatus.

DISCUSSION

Obviously, atmospheric cooling has been utilized to remove the heat of solution. Using sixty-eight pounds of water per carboy, which will give ninety-five pounds of 15 normal ammonium hydroxide it may be calcu-

lated[1] that 23,100 B.t.u. are given off per carboy during the absorption. As absorption takes place, the temperature rises, and less ammonia is absorbed, so that the second carboy has more ammonia to absorb. As the first carboy cools, absorption can increase, but the increasing concentrations of ammonium hydroxide again decrease the rate. The hydrostatic head of solution in the second and third carboys produce a back pressure on the first carboy that increases the concentration. Winter months or rainy weather are better for absorption than hot summer days because of the atmospheric cooling required. No heat was applied to the ammonia cylinder, which drops considerably in temperature as evaporation of liquid ammonia occurs. Heating of the cylinder would give an increased rate of production, due to the more rapid supplying of ammonia to the solution.

The economies effected by this procedure depend upon local costs, particularly freight costs from the manufacturer. In the soft water region, as the Pacific slope, the water contains but little dissolved material, much of which precipitates out during the absorption of the ammonia. Distilled water for the preparation of a pure ammonium hydroxide may be figured at a cost of two-thirds of a cent per gallon.[2]

[1] BICHOWSKY AND ROSSINI, "Thermochemistry of chemical substances," Rheinhold Publishing Company, New York City, 1936.

[2] Barnstead Still and Sterilizer Company, Boston, Massachusetts, Catalog B 1930.

The Thermo-Allotropic Modifications of Sulfur

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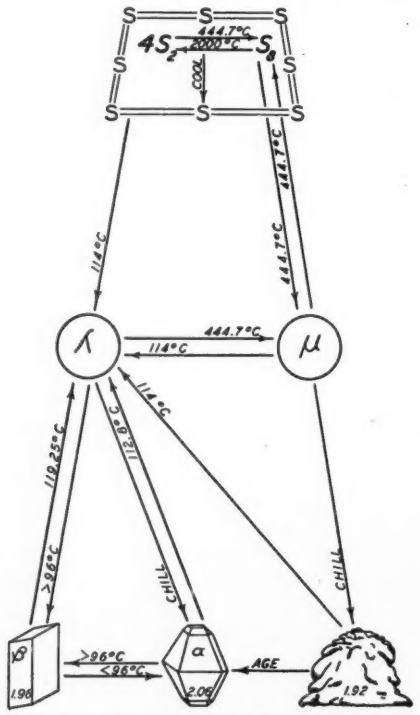
SULFUR, the element that might well be called "The Typical Element," is one of the oldest, cheapest, and doubtless the third most essential elementary substance. Its occurrence and crystal formations appeal to the geologists, many of its approximately one hundred physical properties demand attention from the physicists, its unique method of manufacture in this country stimulates professional pride in the student of chemical engineering, and the numerous fungicidal and germicidal preparations containing sulfur and its compounds prove indispensable to the biologists. The chemist can properly claim a sharing interest in all scientific attainments involving this illustrative element, since chemistry is a science which deals with the properties of matter as they are changed by conditions.



THE THERMO-ALLOTROPIC MODIFICATIONS OF SULFUR (THE CHEMICAL SULFUR DERRICK)

Sulfur, carbon, oxygen, phosphorus, arsenic, selenium, tin, antimony, tellurium, and boron are conspicuously allotropic; most of the heavy metals (with the exception of mercury) show some evidence of allotropy. *Allotropy* is the isomerism of a chemical element which may occur in different interchangeable amorphous and crystalline forms, yet having identical chemical properties. *Isotopy*, a term often confused with allotropy (by the beginning chemistry student), is the existence of very nearly allied but chemically nonseparable forms of some elements, the general chemical properties being identical but exhibiting variations in their atomic weights or masses; *i. e.*, 32, 33, 34 for sulfur.

The thermal conditions necessary for the interchanging of the seven thermo-allotropic modifications of sulfur may be expressed diagrammatically by the *chemical sulfur derrick*, showing simultaneously many other pedagogically digestible facts about this versatile element. The systematic and logical correlation of facts is of primary concern to an alert teacher of a science so general and voluminous as chemistry, so that he may present a long, intricate story in a vivid manner.

Detection of Cadmium

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IN THE systematic analysis of the Group II metals by the hydrogen sulfide method a number of schemes have been used for the separation of cadmium from copper. These, in general, can be divided into (1) systems depending upon the depression of ion concentration by the formation of complex ions and (2) those depending upon the difference in reduction potential between cadmium and copper ions. Typical of the first is the system of holding copper in solution by the addition of an alkali cyanide to the ammoniacal solution of copper and cadmium ions, followed by precipitation of CdS, thus leaving the $Cu(CN)_3^{-2}$ complex in solution. The same system is exemplified by the method of saturating a strongly acid solution of copper and cadmium ions with NaCl and precipitating CuS from the $CdCl_4^{-2}$ complex. The other principle is used in the precipitation of the copper ion by the addition of iron filings to an acid solution of copper and cadmium ions.

From the teaching point of view any of these methods is satisfactory as each is an example of a principle of wide application. However, for the production of a clean-cut separation, none is entirely satisfactory in the hands of students. The use of the alkali cyanide is not liked by most instructors because of the danger of poisoning (and in this connection the possibility of a severe contact dermatitis[3] as well as general systemic poisoning should not be overlooked), although it is generally agreed that it gives the best separation of any of these methods. When it is used, the presence of even very small amounts of bismuth in the solution will darken the CdS precipitate until it cannot be recognized. If the second method is used it is difficult to maintain the concentration of chloride ion sufficiently high to retain small amounts of cadmium ion in solution, while at the same time precipitating copper completely enough so that it will not interfere with the subsequent precipitation of cadmium. In the use of the third method it is difficult to prevent the dissolution of sufficient iron so that it will not be retained, and a dark precipitate again result upon the addition of H_2S.

The method which we have used with considerable success for two years seems to have been first suggested by R. Biewend[4] in 1902 and has since been mentioned twice in the literature, by W. Geilmann[5] and by van Nieuwenburg and Dulfer.[6] While it has thus been known, and used to some extent, in assay work and as a specific test in drop reactions, for nearly forty years it seems never to have been incorporated into a systematic scheme of analysis. It seems to us that the method has sufficient merit that it should be widely used in systematic analysis.

The operation is as follows: When a blue color is obtained in the ammoniacal solution, indicating copper, the solution is evaporated to dryness. It is not necessary to drive off the ammonium salts, so the evaporation can be carried out over a steam bath with no danger of spattering. Since the test is very sensitive only a two-ml. aliquot of the solution need be evaporated in the macro method of analysis. The whole solution is used in semimicro analysis. The resulting dry salts are mixed with about their own volume of a mixture of approximately equal quantities of anhydrous sodium carbonate and powdered carbon. This mixture is transferred to a small ignition tube—conveniently made from four inches of 7-mm. soft glass tubing—and heated to a dull red. Any cadmium in the mixture will distil up into the cooler portion of the tube and deposit as a gray metallic mirror. In order to make the mirror more easily discernible the tube is cooled, a small particle of sulfur is introduced into the bottom, and the tube is again heated until the sulfur distils up over the mirror. This treatment results in the formation of the orange modification of cadmium sulfide which turns yellow on cooling. The color change is typical of cadmium sulfide. The quantity present may be estimated from the size of the cadmium sulfide deposit as well as from the size of a precipitate, and with equal certainty, as the distillation is essentially quantitative. The only difficulty we have observed in several hundred tests conducted by students has been caused by tubes left so covered with carbon that the mirrors could not be seen.

The chemistry involved in these changes can be represented by the following equations:

$$(1)\quad CdCl_2 + Na_2CO_3 \rightarrow CdCO_3 + 2NaCl$$
$$(2)\quad CdCO_3 \rightarrow CdO + CO_2$$
$$(3)\quad 2CdO + C \rightarrow 2Cd + CO_2$$
$$(4)\quad Cd + S \rightarrow CdS$$

Of course, either copper or bismuth will show the same series of reactions equally well but they are completely separated from cadmium because they will not distil at any temperature which can be obtained with a Bunsen burner or in glass apparatus.

In the opinion of the authors the fact that this procedure is a little unusual in qualitative analysis gives it a very definite advantage from the teaching point of view. It permits a separation by a method fundamentally different from any other used in the pro-

[1] Present address: Illinois Department of Labor, Division of Factory Inspection, 205 West Wacker Drive, Chicago, Illinois.

[2] Present address: McArdle Memorial Laboratory, University of Wisconsin, Madison, Wisconsin.

[3] "Occupation and health," International Labour Office, Geneva, Switzerland, **1930**, Vol. II, p. 647.

[4] BIEWEND, *Berg und Hüttenmännische Zeitung*, **61**, 401 (1902).

[5] GEILMANN, *Z. anorg. Chem.*, **155**, 192 (1926).

[6] VAN NIEUWENBURG AND DULFER, "A short manual of systematic qualitative analysis by means of modern drop reactions," Centen, Amsterdam, Holland, **1933**.

cedures. This involves a discussion of the physical properties of the metals involved, and also of these reactions in the dry way, which are of great commercial importance and with which the student will not otherwise come in contact in the course of the laboratory work.

The Flow Sheet and Material Balance of a Quantitative Experiment[1]

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THE chemist in industry has found it convenient to draw flow sheets which indicate the source, course, state, and final disposal of the various substances in a chemical plant. He has likewise found it desirable to keep a material balance or record of his operations, so that, at any desired step, he may calculate an inventory of the various substances and their states which are present in the various parts or units of his plant. Such flow sheets and material balances, will, of course, be simple or complicated depending upon the complexity of the plant and processes involved. We have found that similar flow sheets and material balances are of great value in assisting the student to follow the course of the several substances entering into a quantitative experiment.

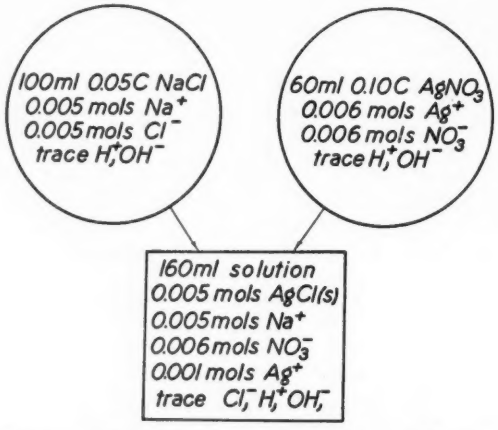

FIGURE 1.—FLOW SHEET FOR PRECIPITATION OF SILVER CHLORIDE

Figure 1 is such a flow sheet representing the precipitation of chloride ion as silver chloride. Circles or ovals are conveniently used to represent materials and their states added, withdrawn, or passing from one vessel to another. Rectangles or rough outlines of the actual equipment are used to represent the various pieces of apparatus. The flow sheet of Figure 1 represents the first approximation in the calculation of the amounts and states of all the substances present.

In setting up the balance sheet or material balance shown in Table 1, we enter the amounts and concentrations of all substances used during the experiment, the substances disappearing in the course of reactions, and the substances appearing as the result of such reactions. As in ordinary bookkeeping, the substances originally present, added during the course of the operation, and formed during the course of reaction, will be entered in a left-hand column. Likewise, the substances disappearing during a reaction or removed from the apparatus for any reason, and the balance of material remaining in the apparatus will be entered in a right-hand column. The entries in Table 1 correspond in many respects to the journal entries of the accountant. In it the several accounts of the several significant substances are in terms of grams (or of mols) while journal entries carry the accounts of the several clients or departments of the business in terms of dollars. The total weight (grams or mols) in the debit column must equal the total weight (grams or mols) in the credit column, just as in ordinary bookkeeping the total value of the debits in dollars must equal the total value of the credits.

TABLE 1
MATERIAL BALANCE OF PRECIPITATION OF SILVER CHLORIDE
(FIRST APPROXIMATION)

	Grams		*Mols*		*Water (l.)*		*Volume*	*C*
Substance	*Dr.*	*Cr.*	*Dr.*	*Cr.*	*Dr.*	*Cr.*	*Liters*	*Mols/l.*
Start: 0.2923 g. NaCl in 100 ml. of water								
Na^+	0.1150		0.005				0.100	0.05
Cl^-	0.1773		0.005				0.100	0.05
Water					0.100			$a = 1$
H^+, OH^-	Traces							
Added: 60 ml. $AgNO_3$ soln., 0.01079 g. Ag^+ per ml.								
Ag^+	0.6473		0.006				0.060	0.10
NO_3^-	0.3720		0.006				0.060	0.10
Water					0.060			$a = 1$
H^+, OH^-	Traces							
Reaction: $Ag^+ + Cl^- = AgCl(s)$								
Ag^+		0.5394		0.005				
Cl^-		0.1773		0.005				
AgCl(s)	0.7167		0.005					$a = 1$
Finish: Balance								
AgCl(s)		0.7167		0.005		0.160		$a = 1$
Na^+		0.1150		0.005			0.160	0.03125
NO_3^-		0.3720		0.006			0.160	0.0375
Ag^+		0.1079		0.001			0.160	0.00625
Water							0.160	$a = 1$
Cl^-, H^+, OH^-	Traces							
	2.0283	2.0283	0.027	0.027	0.160	0.160		

[1] All rights reserved. See RANDALL AND YOUNG, "Elementary applications of physical chemistry," (*In preparation*).

Such material balances may be made either in grams or in mols. In general, the mol is a much more convenient unit for this purpose, since it is much easier to make the stoichiometric calculations in terms of mols rather than grams. We have found it convenient, at the outset, to use both mols and grams as is indicated in our table. It is not very long, however, until the student becomes so impressed with the simplicity of the mol as a unit of mass, that he immediately converts any amounts given in grams into mols, and thereafter uses mols exclusively.

For convenience in calculating concentrations, it is convenient to make the account or balance for the solvent in separate debit and credit columns. This solvent balance may be kept either in terms of liters as indicated in Table 1 or in terms of grams times 10^3 if one is interested in calculating concentrations as molalities. For convenience in making further calculations, we have added in the last column of Table 1 notations giving the state, that is, the concentrations, mols per liter, or activities of the several substances entered in the balance. For convenience in making the calculations of the concentrations, we have also entered a column giving the total volume of solvent present at the given entry.

A sample of sodium chloride, *e. g.*, 0.2923 g. or 0.005 mol, is dissolved in 100 ml. of water. The beaker now contains 0.100 l. of water, 0.1773 g. of chloride, 0.1150 g. of sodium ion. We therefore debit the experiment with these substances. Very small amounts of hydrogen ion and of hydroxyl ion are also present. The concentration of the sodium ion and of the chloride ion in the solution is 0.005 mol per 0.100 liter, or, more conveniently, 0.05 mol per liter.

If we now add 60 ml. of silver nitrate solution containing 0.01079 g. or 0.0001 mol of silver ion per ml. to this solution, we must debit these substances in our balance sheet. The silver nitrate solution contains traces of hydrogen and hydroxyl ion. As a first approximation we may assume that all the chloride ion present will combine completely with silver ion. Assuming that this reaction is complete, we must credit in our balance sheet for the disappearance of 0.005 mol of silver ion and 0.005 mol of chloride ion, and likewise debit our balance sheet with the appearance of 0.7167 g. or 0.005 mol of solid silver chloride.

We therefore find the amounts of the various substances in the beaker at the end of the experiment by entering on the credit side 0.005 mol of sodium ion, 0.006 mol of nitrate ion, 0.001 mol of silver ion, and 0.005 mol of solid silver chloride.

As a check upon the accuracy of the balance sheet the total of the amounts in each pair of the debit and credit columns must be the same. Likewise the total amount of the various classes of substances, *e. g.*, Ag^+, AgCl, etc., must be the same in each pair of debit and credit columns.

If we were concerned with a very complicated reaction, we might prepare separate accounts or balances for such of these substances for which it might prove convenient to have separate accounts. That is, separate pairs of debit and credit columns, as has been done in the case of the water, are used for important substances.

We cannot say that the silver chloride is entirely insoluble in the solution, although the amount of chloride ion remaining in the solution must be exceedingly small. We may, however, on the basis of the concentration of the silver ion (first approximation) shown in the balance sheet, make a calculation (second approximation) of the amount of chloride ion remaining in solution.

$$\begin{aligned} &AgCl(\text{solid}, a = 1) = Ag^+ + Cl^- \\ &K = m(Ag^+)m(Cl^-)/1 = 1.73 \times 10^{-10} \end{aligned} \qquad (1)$$

We thus find the concentration of chloride ion by substituting

$$\text{in equation (1), whence } \begin{matrix} c(Ag_+) = 0.00625 \\ c(Cl^-) = 2.77 \times 10^{-8} \end{matrix}$$

The volume is given in Table 1; hence we may calculate the amount of chloride ion in grams or mols (4.43×10^{-9} mols). Now in Table 1 (first approximation) we assumed that the reaction for the precipitation of silver chloride was complete. In other words, the first approximation assumes that too much silver ion (the number of mols corresponding to the number of mols of chloride ion remaining in solution) was used up. Hence the amount of silver ion should have been

$$0.001 + 4.43 \times 10^{-9} \text{ mols}$$

We may now make a third approximation. The new concentration of the chloride ion is 2.768×10^{-8}, which does not differ by a significant amount from the second approximation and may therefore be considered to be the true concentration of chloride ion remaining in the solution.

Just as in the case of an industrial process, the analyst wishes to know the experimental error or loss in his procedure. Here the fractional loss due to incomplete precipitation is obviously $4.43 \times 10^{-9}/0.005$ mols or 0.89×10^{-5} per cent.

TABLE 2.
JONES REDUCTOR

	Mols		Water (l.)		Volume	C
Substance	*Dr.*	*Cr.*	*Dr.*	*Cr.*	*Liters*	*Mols/l.*
Start: 50 ml. of 0.05 *C* $Fe_2(SO_4)_3$, 0.2 *C* H_2SO_4						
Fe^{+++}	0.005		0.050		0.050	0.10
H^+	0.020				0.050	0.40
SO_4^{--}	0.0175				0.050	0.35
Added: 150 ml. of 0.5 *C* H_2SO_4 and Zn						
H^+	0.150		0.150		0.150	1.0
SO_4^{--}	0.075				0.150	0.5
Zn(s)	0.0025					$a = 1$
Reaction: $2Fe^{+++} + Zn(s) = 2Fe^{++} + Zn^{++}$						
Fe^{+++}		0.005				
Zn(s)		0.0025				
Fe^{++}	0.005					
Zn^{++}	0.0025					
Balance Leaving Jones Reductor (First Approximation)						
Fe^{++}		0.005		0.200	0.200	0.025
Zn^{++}		0.0025			0.200	0.0125
Fe^{+++}		Trace				
H^+		0.17			0.200	0.85
SO_4^{--}		0.0925			0.200	0.4625
	0.2775	0.2775	0.200	0.200		

Figure 2 shows a flow sheet for the reduction of a sample of ferric ion in a Jones reductor and its subsequent titration with acid permanganate solution. Table 2 shows the material balance for the reduction step and Table 3 the corresponding material balance for the titration step.

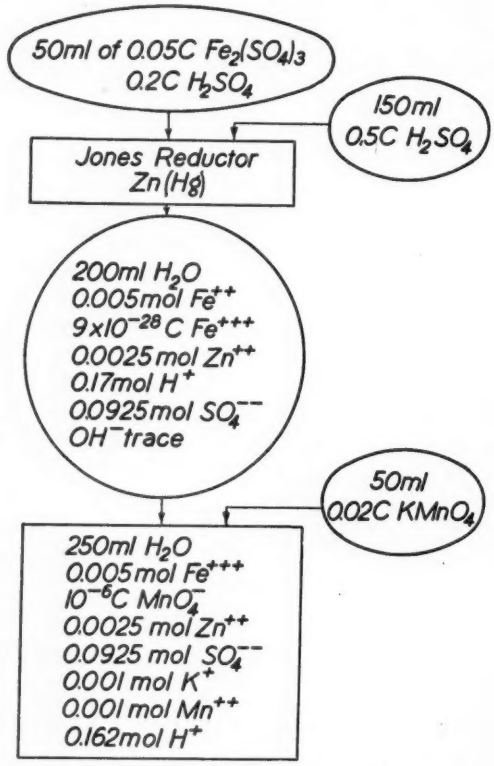

FIGURE 2.—FLOW SHEET FOR JONES REDUCTOR AND TITRATION WITH PERMANGANATE SOLUTION

The equilibrium constant of the significant reaction in the Jones reductor is

$$2Fe^{+++} + Zn(s) = 2Fe^{++} + Zn^{++}$$
$$K = c^2(Fe^{++})c(Zn^{++})/c^2(Fe^{+++}) = 7.5 \times 10^{50} \qquad (2)$$

Substituting the approximate activities of Fe^{++}, Zn^{++}, and Zn(s) from Table 2 we find the molality of the ferric ion remaining unreduced to be 10^{-28}, or the ferrous ion not reduced is 4×10^{-25} per cent. Such a calculation of course does not take into account the possibility that the reaction in the Jones reductor might not have reached equilibrium.

We find that it is possible to observe a concentration of permanganate ion not greater than 2×10^{-6} *C*. From tables of the standard electromotive force of half cells we find the approximate equilibrium constant

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O(l.)$$
$$K = c^5(Fe^{+++})c(Mn^{++})/[c^5(Fe^{++})c(MnO_4^-)c^8(H^+)] = 2.3 \times 10^{65} \qquad (3)$$

Taking the approximate values of the activities of the several ions remaining at the end of the titration from Table 3, we find that with the hydrogen ion present in our experiment, the concentration of the ferrous ion is 2×10^{-14} corresponding to 10^{-11} per cent unoxidized ferrous ion. A second approximation is identical with the first.

TABLE 3
PERMANGANATE TITRATION

	Mols		Water (l.)		Volume	C
Substance	*Dr.*	*Cr.*	*Dr.*	*Cr.*	*Liters*	*Mols/l.*
Leaving Jones Reductor:						
Fe^{++}	0.005		0.200		0.200	0.025
Zn^{++}	0.0025					0.0125
H^+	0.17					0 85
SO_4^{--}	0.0925					0.4625
Added in titration to theoretical end point: 50 ml. 0.02 *C* $KMnO_4$ soln.						
K^+	0.001		0.050		0.050	0.02
MnO_4^-	0.001				0.050	0.02
Added as indicator: 2×10^{-6} *C* $KMnO_4$						
K^+	0.0000005				0.250	2×10^{-6}
MnO_4^-	0.0000005				0.250	2×10^{-6}
Reaction: $5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$						
Fe^{+++}		0.005				
MnO_4^-		0.001				
H^+		0.008				
Fe^{++}	0.005					
Mn^{++}	0.001					
Balance: At end of titration						
Fe^{++}		0.005		0.250	0.250	0.020
Zn^{++}		0.0025			0.250	0.010
Mn^{++}		0.001			0.250	0.004
K^+		0.0010005			0.250	0.004
H^+		0.162			0.250	0.648
SO_4^{--}		0.0925			0.250	0.370
MnO_4^-		0.0000005			0.250	2×10^{-6}
	0.278001	0.278001	0.250	0.250		

We may calculate the concentration of hydrogen ion which must be present in order to oxidize the ferrous ion with an error no greater than 0.1 per cent. By reference to Table 3, we find that the concentration of the ferric ion is 0.020. The concentration of the ferrous ion must therefore be not greater than 0.000002 *C*. Now substituting in equation (3) we find that the concentration of hydrogen ion must be greater than 10^{-6} *C*.

Use of these illustrations has established the value and convenience of these material balances and flow sheets. They aid the student in visualizing just what is happening in quantitative experiments. They also aid greatly in removing a certain element of uncertainty concerning the way of obtaining concentrations used in the solution of problems involving equilibrium constants in aqueous solutions. It is obvious that the more complicated the problem, the more useful these aids become.

The authors wish to acknowledge their indebtedness to Dr. Bruce Longtin for valuable suggestions.

Labels in Calculations of Quantitative Chemical Analysis

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RESULTS of quantitative chemical analyses are derived from experimental measurements by application of established chemical, physical, and mathematical principles. The derivation ordinarily requires some type of calculation. The calculation does not deal with abstract numbers, as is the case in purely mathematical problems, but involves definite physical entities.

Many textbooks do not stress this fact. Illustrative problems contain only numbers in the calculations, but the answers are given in definite units. Often, even the answers are abstract. It is not only illogical but also poor pedagogy to equate pure numbers to terms having dimensions. The displayed equation should be dimensionally homogeneous. An abstract equation should not be used to represent relations between measurements of properties. More emphasis ought to be placed on the use of units and designation of materials in chemical calculations.

Students taught to use units and to think in terms of dimensions seem to master chemical calculations more readily than those who have not been thus trained. Units give numbers physical meaning. Desired relations between measurements are clearer and more easily understood. The budding chemist who does not use units usually produces a formula from memory or text, makes a numerical substitution and solves. He hopes that the written or mental formula applies to the problem, that the numerical relations are correct, and that the units assigned to the result are right. If the units are carried through the calculation process, the relations will be shown to be correct or incorrect, and the units of the answer will be determined. Much uncertainty will be eliminated.

A few beginners are reluctant to label all numbers used in calculations by naming all units and materials. Some of the reasons given are: Why waste time writing down anything besides the numerical portion of the data? The figures substituted in the correct formula give the desired numerical answer. After all, this is the most important part of the result. If the statement of the problem does not include the appropriate label for the answer, it can be figured out very easily. Why doesn't the text use labels? This attitude is natural if the student has neither grasped the fundamental concepts of units and dimensions nor realized the benefits gained by their use.

Most teachers and texts of quantitative chemical analysis introduce to the student the principles of precision, error, and significant figures. Units and dimensions should be included in the introduction.[1] He should be shown the logical necessity and advantages gained by the use of labels in problems. In a chemical calculation, the treatment of units is just as important as the handling of significant figures.

The simple fundamentals serve as a starting point for a brief, elementary discussion on the use of units, dimensions, and labels. Chemical analysis requires the direct or indirect measurement of certain properties of matter. The measurements are compared to or scaled with reference standards. These standards are usually called "units." The property or quantity measured is described in terms of "dimensions."

For example, suppose the property measured is density. The dimensions of density are mass/volume. The units used for scaling may be grams/milliliter or perhaps pounds/cubic foot. The property in question might be length. The dimension is length. The unit may be meter or yard.

As soon as the measurement is completed, it is recorded. The record should include the following:

(1) Designation of material used.
(2) Name of property or quantity measured.
(3) Reference standard or unit used.
(4) Number value indicating how many times the unit is contained in the quantity measured.

Consider the weighing of a sample of soda ash on the analytical balance. The record of the measurement reads "weight of soda ash = 4.1567 grams" or "mass = 4.1567 grams of soda ash." The data show that the material is soda ash, the property is mass, the unit is gram, and 4.1567 of these units are contained in the amount of material measured.

Properties that are uniquely described by the units used or by the experimental record do not have to be named. All other properties must be designated. In the above example, "4.1567 grams of soda ash" is sufficient because the gram unit uniquely fixes the property measured as mass. The name or dimension of the property may be omitted from the record.

(The process of measuring mass by the aid of the analytical balance is called "weighing." Thus the chemist ordinarily uses the term "weight" when referring to the measurement. Actually, weight is a force in which the acceleration factor is due to gravity. The weight of the unit mass is often employed as a unit of force. The gravitational unit of force in the metric

[1] A good brief discussion on units and dimensions is given by MACK AND FRANCE. References are included (*1*).

system is the weight of one gram mass, written "one gram weight.")

Analysts use the metric system (C.G.S.) of measurement. The fundamental reference standards of the system are defined as follows (*2*):

The primary standard of length is the distance between two lines at 0°C. on a platinum-iridium bar known as the International Prototype Meter deposited at the International Bureau of Weights and Measures. [The centimeter (cm.) is a secondary standard of length derived from the meter.]

The primary standard of mass is the mass of the International Prototype Kilogram of platinum-iridium kept at the International Bureau of Weights and Measures at Sevres. (The gram is a secondary standard derived from the kilogram.)

The primary standard of time is the mean solar second, one eighty-six thousand four hundredth (1/86,400) part of a mean solar day.

The standard scale of temperature adopted by the International Committee of Weights and Measures is defined by taking the temperature of melting ice as 0° and that of condensing steam as 100°. The pressure at which the measurements are made is 760 mm. of mercury. This is known as the Centigrade (C.) scale.

Two derived standards of volume or capacity are used by chemists. The unit adopted by the analyst is the liter. The liter is defined as the volume occupied by a mass of one kilogram of pure water (*3*) at its maximum density and under a pressure of 760 mm. of mercury (*4*). The liter is derived from the fundamental reference standard of mass, the kilogram. The other unit is the cubic meter which is defined on the basis of the primary standard meter. This unit is derived from the fundamental reference standard of length. The liter equals 1.000028 cubic meters (*5*).

Three chemical units of mass are ordinarily used in analytical measurements.

(1) The mol is the molecular or formula weight of a substance expressed in grams. The millimol (m.mol) is 1/1000 of a mol.

Example:

40.01 g. NaOH = 1 mol NaOH; 40.01 mg. NaOH = 1 m.mol. NaOH

(2) The equivalent is the mass of a substance in grams which will react directly or indirectly with 8.0000 grams of oxygen or 1.0081 grams of hydrogen (naturally occurring isotopic mixtures) (*3*). The milliequivalent is 1/1000 of an equivalent.

Example:

40.01 g. NaOH = 1 equivalent NaOH; 40.01 mg. = 1 meq. NaOH

(3) The equivalency (*6*) is the mass of a substance in grams which will react with or is chemically equivalent to one milliliter (or one gram) of the standard solution.

Example:

0.005 g. NaOH reacts with 1 ml. HCl solution.

$\frac{0.005 \text{ g. NaOH}}{1 \text{ ml. HCl soln.}}$ is the NaOH equivalency of the solution.

The record of a measurement should be completely and specifically labeled. The label consists of the correct units and the designation of the material used. The label of "10 ml. HCl soln." is "ml. HCl soln."

Measurements used in calculations should be labeled. The labels are treated just as the numbers involved: *i. e.*, multiplied and canceled along with the numerical terms in the expression. A calculation in which labels are used might be called a "numerical–label" calculation.

Including labels in a calculation is definitely advantageous. The advantages may be listed as follows:

(1) Each term has a definite physical meaning. The property and material referred to by the term is ascertained at once from the calculation.

(2) If the label of the answer is known, the correct setup of the calculation may be obtained by the trial and error method.

(3) The labels serve as a check on the setup of the problem.

Consider a simple calculation involving an HCl solution whose density is $\frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}}$ and whose volume is 10 ml. HCl soln.

(1) $1.1 \times 10 = 11$. The terms have no physical meaning. They are merely abstract numbers. No one can tell what the problem involves by looking at the above equation. But if the terms are labeled:

$$\frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}} \times 10 \text{ ml. HCl soln.} = 11 \text{ g. HCl soln.}$$

Each term has a meaning. The equation is no longer abstract.

(2) If the mass of the HCl solution is desired, which of the following relations is the one to use? 1.1×10; $1.1/10$; $10/1.1$? The answer is not obtained by looking at the terms unless they are labeled.

$$\frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}} \times 10 \text{ ml. HCl soln.}$$

$$\frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}} \div 10 \text{ ml. HCl soln.}$$

$$10 \text{ ml. HCl soln.} \div \frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}}$$

As the answer label desired is "g. HCl soln.," the correct setup for the calculation is readily seen to be the first. The answer label for the second is

$$\frac{\text{g. HCl soln.}}{(\text{ml. HCl soln.})^2}$$

and for the third is

$$\frac{(\text{ml. HCl soln.})^2}{\text{g. HCl soln.}}$$

(3) Suppose the problem is set up as 1.1/10. Is the relation correct to solve for mass of solution? The labels answer the question at once.

$$\frac{1.1 \text{ g. HCl soln.}}{1.0 \text{ ml. HCl soln.}} \div 10 \text{ ml. HCl soln.} \neq \text{g. HCl soln.}$$

The relation is shown to be incorrect.

Perhaps it will be helpful to formulate the simpler

types of titrimetric calculations and substitute appropriate units in the formulas. Relations between the units in certain problems are then clearly shown.

(1) Solution density $\times \frac{\text{constituent \%}}{100\ \%}$ = constituent concn.

$$\frac{\text{g. soln.}}{\text{ml. soln.}} \times \frac{\text{g. constituent}}{\text{g. soln.}} = \frac{\text{g. constituent}}{\text{ml. soln.}}$$

(2) $\frac{\text{Concn. constituent}}{\text{Millimol}}$ = molarity

$$\frac{\text{g. constituent/ml. soln.}}{\text{g. constituent/m.mol constituent}} = \frac{\text{m.mol constituent}}{\text{ml. solution}}$$

(3) $\frac{\text{Concn. constituent}}{\text{Milliequivalent}}$ = normality

$$\frac{\text{g. constituent/ml. soln.}}{\text{g. constituent/meq. constituent}} = \frac{\text{meq. constituent}}{\text{ml. solution}}$$

(4) Normality $\times$ milliequivalent = equivalency

$$\frac{\text{meq. constituent}}{\text{ml. std. soln.}} \times \frac{\text{g. constituent}}{\text{meq. constituent}} = \frac{\text{g. constituent}}{\text{ml. std. soln.}}$$

(5) $\frac{\text{Weight constituent titrated}}{\text{Vol. std. soln. used}}$ = equivalency of std. soln.

$$\frac{\text{g. constituent}}{\text{ml. std. soln.}} = \frac{\text{g. constituent}}{\text{ml. std. soln.}}$$

(6) Molarity $\times$ volume = number millimols of constituent

$$\frac{\text{m. mol constituent}}{\text{ml. solution}} \times \text{ml. solution} = \text{m. mol constituent}$$

(7) Normality $\times$ volume = number milliequivalents constituent

$$\frac{\text{meq. constituent}}{\text{ml. solution}} \times \text{ml. solution} = \text{meq. constituent}$$

(8) $\frac{\text{Weight constituent}}{\text{Weight of sample}} \times 100\%$ = percentage of constituent

$$\frac{\text{g. constituent}}{\text{g. sample}} \times 100\ \text{g. sample} = \text{g. constituent}$$

(9) $\frac{\text{Vol. std. soln.} \times \text{constit. equivalency} \times 100\%}{\text{Weight of sample}}$ = constituent %

$$\frac{\text{ml. std. soln.} \times \text{g. constituent/ml. std. soln.} \times 100\ \text{g. S.}}{\text{g. S.}} = \text{g. constituent}$$

(10) $\frac{\text{Vol. std. soln.} \times \text{normality} \times \text{milliequiv.} \times 100\%}{\text{Weight of sample}}$ = % constituent

$$\frac{\text{ml. std. soln.} \times \frac{\text{meq. constit.}}{\text{ml. std. soln.}} \times \frac{\text{g. constit.}}{\text{meq. constit.}} \times 100\ \text{g. S.}}{\text{g. S.}} = \text{g. constituent}$$

The use of labels in a typical titrimetric problem is illustrated by the following example (7).

"A sample of 3.500 g. soda ash was diluted to 250.0 ml. of solution. If a 25.00 ml. aliquot required 30.00 ml. sulfuric acid solution containing 0.006000 g./ml. when titrated in the presence of methyl orange, calculate the per cent purity of the sample."

Solution:

$$\frac{0.006000\ \frac{\text{g. } H_2SO_4}{\text{ml. } H_2SO_4 \text{ soln.}}}{0.04904\ \frac{\text{g. } H_2SO_4}{\text{meq. } H_2SO_4}} = 0.1168\ \frac{\text{meq. } H_2SO_4}{\text{ml. } H_2SO_4 \text{ soln.}} = \text{normality}$$

$$30.00\ \text{ml. } H_2SO_4 \text{ soln.} \times 0.1168\ \frac{\text{meq. } Na_2CO_3}{\text{ml. } H_2SO_4 \text{ soln.}} \times 0.0530\ \frac{\text{g. } Na_2CO_3}{\text{meq. } Na_2CO_3} \times 100\ \text{g. soda ash} \div 3.500\ \text{g. soda ash} \times \frac{25.00\ \text{ml. soda ash soln.}}{250.0\ \text{ml. soda ash soln.}}$$

= 55.58 g. Na_2CO_3 in 100 g. soda ash,[2] or 55.58% purity

An excellent method for the solution of chemical, physical, and engineering problems is the "factor label" or "factor" method taught by Professor F. D. Martin in all general chemistry classes for freshman engineers at Purdue University (*8*). The solution is obtained by the operation of appropriate conversion factors on the given measurement. The solution of the above example by this method would be:

$$\text{? g. } Na_2CO_3 = 100\ \text{g. soda ash} \times \frac{250.0\ \text{ml. soda ash soln.}}{3.500\ \text{g. soda ash}} \times \frac{30.00\ \text{ml. } H_2SO_4 \text{ soln.}}{25.00\ \text{ml. soda ash soln.}} \times \frac{0.006000\ \text{g. } H_2SO_4}{1\ \text{ml. } H_2SO_4 \text{ soln.}} \times \frac{106.0\ \text{g. } Na_2CO_3}{98.08\ \text{g. } H_2SO_4}$$

= 55.58 g. Na_2CO_3 in 100 g. soda ash, or 55.58% Na_2CO_3

As a typical gravimetric calculation, consider the following problem.

"A 0.5000 g. sample of magnetite iron ore yields 0.4000 g. Fe_2O_3. What is the percentage of iron in the ore?"

Solution:

$$\frac{0.4000\ \text{g. } Fe_2O_3 \times \frac{111.68\ \text{g. Fe}}{159.68\ \text{g. } Fe_2O_3} \times 100\ \text{g. ore}}{0.5000\ \text{g. ore}}$$

= 13.99 g. Fe in 100 g. ore, or 13.99% Fe

The factor method of solution would be:

$$\text{? g. Fe} = 100\ \text{g. ore} \times \frac{0.4000\ \text{g. } Fe_2O_3}{0.5000\ \text{g. ore}} \times \frac{111.68\ \text{g. Fe}}{159.68\ \text{g. } Fe_2O_3}$$

= 13.99 g. Fe in 100 g. ore, or 13.99% Fe

The labeling of each term requires a little more time, takes up a little more space and may seem unnecessary. It will pay dividends to the student who forms the habit of labeling and carrying the labels through each operation of the calculation. These dividends will be a clearer understanding of chemical and physical calculations and the number of problems solved correctly. The teacher who demands the use of labels will probably discover that the interesting but difficult task of teaching chemical calculations to the slower student becomes easier. These statements apply not only to the subject of quantitative chemical analysis but also to general chemistry and all other courses in chemistry, physics, and engineering.

[2] If labels are used, "100 g. sample" is substituted for "100%." The student soon realizes the significance of the word "percentage" or the term "per cent." In a calculation of the above type it means the weight of the constituent in 100 parts by weight of sample.

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A Rapid Method of Correcting for Inequality of Beam Arms in the Analytical Balance

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IN PROCEDURES requiring absolute weights it often becomes necessary to correct for the inequality of the beam arms of the balance. Two methods which are stressed in textbooks of chemistry are double weighing and weighing by substitution. A third method consists of determining the ratio of the lengths of the arms and multiplying relative weights by this factor. A fourth method which has been overlooked to a great extent is, according to Krayer,[1] "adding or subtracting the amount of the error, or changing the theoretical zero point on the index plate." This method, once the necessary data have been gathered, is by far the most rapid.

[1] KRAYER, "The use and care of a balance," The Chemical Publishing Co., Easton, Pa., **1913**.

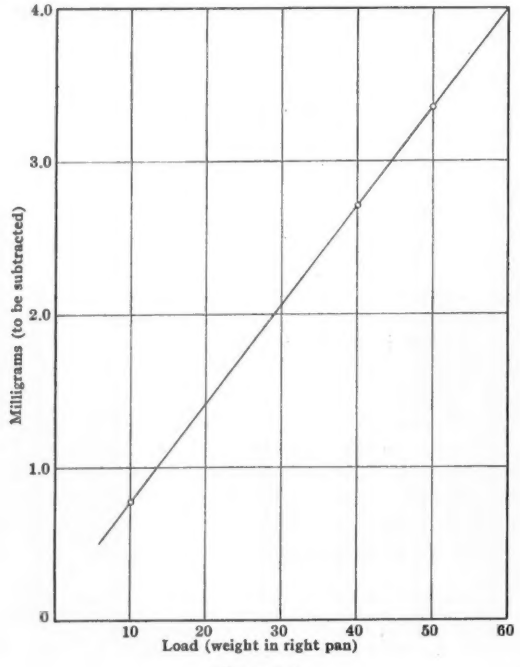

FIGURE 1

It has been found particularly advantageous to plot the correction in milligrams against the load, and to read from this curve, at the completion of each weighing, the number of milligrams which must be subtracted (or added) to obtain absolute weight. The zero point is employed as determined.

The following considerations relate to the nature of the curve. By the law of levers,

$$W_l L = W_r R \tag{1}$$

where W_l is the absolute weight in the left pan, L is the length of the left beam arm of the balance, W_r is the weight on the right pan, numerically the relative weight of the object, and R is the length of the right beam arm. Equation (1) may be written.

$$\Delta W = W_l - W_r = (R/L - 1)W_r \tag{2}$$

Setting M equal to $(R/L - 1)$ and substituting, equation (2) becomes

$$\Delta W = MW_r \tag{3}$$

which is the equation of a straight line passing through the origin. If the ratio R/L varies with load, as it may, the line will curve slightly.

The following method may be employed in obtaining the correction curve. The zero point for the empty balance is determined. Ten-gram weights which have been calibrated relative to each other by the method of weighing by substitution are placed in the right and left pans, and by the use of the chain or rider the original zero point is obtained. After the inequality of the weights has been compensated for, the reading gives the correction for the unequal beam arms for the ten-gram load and its direction. If the zero point tends to come to the right, the correction is to be subtracted and vice versa. The same procedure, employing two twenty-gram weights, and again with two fifty-gram weights, establishes the curve. One point lies at the origin. The correction curve for the author's balance is shown in Figure 1.

I am indebted to Dr. E. I. Fulmer for suggestions concerning this paper.

HIGH-SCHOOL NOTES

The Curriculum in Secondary Chemistry in Relation to the Needs of American Youth

R. A. EADS

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THE period since 1920 is epochal in American education. This period is characterized by a new educational philosophy, general dissatisfaction with educational conditions, a shifting of emphasis from the subject to the child, survey movement, tests and measurements movement, attempts to differentiate to meet individual pupil needs and local community needs, the curriculum movement, and an unprecedented number of publications on every phase of modern school life.

In short, the straight-laced, mastery-of-subject-matter, college-preparatory school was under fire. It no longer satisfied the needs of American youth and our new, increasingly complex social order.

The aims of education during this period centered around the theme of citizenship. General and specific aims were set up for both elementary and secondary schools, for the separate grades and for the various subjects. Subjects were not to be mastered for the sake of mastery. They were to be taught in relation to actual interests and needs of the child, present and future.

TRADITIONAL CONTENT IN CHEMISTRY

Significant is the fact that while much improvement has been made in method and in application of school subjects to life situations, there has been surprisingly little change in actual content of high-school subjects. Particularly is this true of chemistry. Scientific investigation has enriched both our college and high-school courses in chemistry by additions of new material, but we have not discarded an equal amount of material. Consequently, our course in high-school chemistry has become too crowded for effective teaching.

Considerable improvement has been made in methods of presentation, in applications to life situations, and in differentiation to meet individual pupil needs, but the content is essentially the same as in 1915 and derived from the same source, namely, chemistry courses designed for use in colleges.

Formulators of high-school courses in chemistry have used college courses as patterns and have produced courses too similar to them in content and difficulty, as the quotations below will show.

The following is taken from a widely used high-school text, written in 1925, revised in 1931, and reprinted in 1935:

> PREFACE TO SECOND EDITION
>
> This revised edition was undertaken for the purpose of bringing the text thoroughly up to date. The subject matter on the structure of atoms has been completely changed and enlarged. It includes a brief history of the electronic theory of the structure of matter, and an adequate treatment of the atom according to the Bohr theory, including valence, isotopes, and polar and non-polar compounds. Among other topics which have received consideration are the structure of salt crystals; fertilizers; helium; foods, including vitamins, and the processes of digestion and assimilation; oxidation and reduction from the point of view of the electronic theory, and many other minor changes.
>
> A new chapter (XLI) has been added on the recent developments in chemistry and their applications. It is felt that this chapter will be interesting and profitable to both teachers and pupils.
>
> 1931 E. L. D.

The following chapter headings were found to be common to three texts, each widely used, one written in 1907, one in 1915, and the other in 1934: (1) Gas Measurement, (2) Oxygen, (3) Hydrogen, (4) Water, (5) Atomic and Molecular Theories, (6) Chlorine, (7) Hydrochloric Acid, (8) Atomic and Molecular Weights, (9) Symbols and Formulas, (10) Sodium and Potassium Compounds, (11) Sulfur and Sulfides, (12) Oxides and Acids of Sulfur, (13) Nitrogen and the Atmosphere, (14) Nitrogen and Its Compounds, (15) Halogens, (16) Carbon, (17) Oxides of Carbon, (18) Calcium and Its Compounds, (19) Periodic Law.

The text of 1907 contained thirty-five chapters, the one for the year 1915, forty, and the text for 1934 contained forty-one chapters with a nine-division Appendix.

The similarity of these texts is even greater than the chapter headings indicate. They each treated all the common metals, but grouped them differently, giving rise to different chapter headings. While in reality the subject matter covered is very similar, a difference noted in these texts seems to be characteristic of the changes in high-school chemistry texts.

The text for the year 1915 contained chapters not given in 1907, such as: Iron and Steel, Industrial Carbon Compounds, and Radium and Radioactivity. The text for 1934 included these and added: Colloids, Alloys, Cement-Porcelain-Glass, and Photochemistry.

The foregoing shows not only that the content has not changed appreciably; it shows also that the organization is still based on subject matter. The chapter is still the principal basis of organization. Those who claim to have organized subject matter into *units* have merely grouped a number of more or less related chapters together and styled the groups *units*, without attempting any significant changes of subject matter reorganization within the chapters.

A survey of recent courses of study in chemistry reveals the same subject matter organization and essentially the same sequence as found in high-school and

college texts on chemistry, showing clearly that the source of material for course of study construction is the text on general chemistry.

The curriculum movement has had but little, if any, effect on high-school course of study production in chemistry. Miss Ruth Reed, for her thesis "Some Recommendations Concerning Secondary-School Chemistry" (University of Texas, 1935), examined twenty-two representative courses of study representing principal states and cities in the United States. Quoting Miss Reed, ". . . in only two or three of the courses of study examined has there been an attempt to adjust to the concepts of curriculum trends."

THE TEXAS PROGRAM OF CURRICULUM REVISION IN CHEMISTRY

The philosophy underlying the curriculum revision in secondary chemistry in Texas is no different from that underlying the statewide curriculum movement. Doctor Fred C. Ayer, Professor of Educational Administration, University of Texas, and Consultant for the Texas Curriculum Committee, has aptly stated the philosophy underlying the curriculum revision movement in Texas:

1. The curriculum shall provide educative experiences adapted to the fundamental needs of each child of whatever race, type, or mental aptitude.
2. The curriculum shall provide educative experiences for effective participation in social life and which will serve to perpetuate and improve the ideals and practices of our democratic society.
3. The curriculum shall be conceived as a body of dynamic experiences.
4. The curriculum shall be conceived as a program of study and activity subject to teacher guidance.
5. The curriculum revision program shall be conceived as an experimental program.
6. The curriculum shall not be subverted to special interests.

The revision of the secondary-school course in chemistry is a part of the general revision program. If chemistry is to do its part in preparing American youth to live happily and securely in this increasingly complex civilization, it must undergo fundamental revision, if not reconstruction. The teachers of chemistry in Texas, as elsewhere in the United States, are lagging far behind many other subject specialists in meeting the demands of society for functional content in high-school courses. The average secondary course in chemistry is highly theoretical, abstract, uninteresting, and presents logically organized factual data with but little regard for the needs of the pupil.

The teaching chemist should lead in this revitalizing movement in our public schools. No other subject offers such a varied field of vital, functional content.

The Texas curriculum revision program was initiated under the direction of Doctor W. A. Stigler. The leaders in this statewide curriculum movement set up new objectives, devised new methods of selecting content, selected a different basis of organization, and built up a tentative course of study consisting of several wide areas, each broken down into units. Local teachers are advised to select the materials as local interests and needs demand and that local equipment permits.

The following objectives in teaching high-school chemistry are taken in part from *Teaching Science*, a state department bulletin, No. 383, and in part from a recent unpublished manuscript by the writer:

1. To reveal the fascinating phenomena of chemistry.
2. To reveal the chemical reactions in a few of our simpler body functions.
3. To reveal the role of chemistry in such important processes as: cooking, preserving foods, plant growth, sanitation, health, fires, burns, decay, poisons, medicine, and first aid.
4. To learn how to detect fraudulent and misleading advertisements.
5. To learn to judge properly, or at least question, values, particularly of synthetic foods and drugs.
6. To learn the effects of alcohol, narcotics, and tobacco on the human system.
7. To acquire sufficient vocabulary to be able to read intelligently and to converse with informed people.
8. To reveal the role of chemistry in American industry.

We have departed from the usual methods in the selection and organization of content. We have undertaken the determination of content by objective methods.

The selection of material is based on the axiomatic statement: "Every child needs to have at least an elementary knowledge of the chemistry involved in the experiences that are common to every child." Our task then was first to set up procedures to determine those vital experiences common to every child, and to select the requisite amount of subject matter to give the child an adequate and intelligent understanding of such experiences.

We have made analyses of experiences common to child and adult life as revealed by: (1) recent educational research, (2) popular magazines, (3) public press, (4) experiment station literature, and (5) daily life habits.

We have also made use of courses of study, recent texts, and opinions of experts, but the predominant factors in selection have been:

1. Experiences of child and adult life.
2. Current use of chemistry as revealed by current periodicals and the public press.

The Texas curriculum program is now under the direction of Doctor E. H. Hereford, who is carrying out the program under a serious handicap of limited funds. Doctor Hereford plans to publish soon a bulletin outlining content for the guidance of Texas teachers in the field of secondary sciences.

This bulletin will list functional units, or areas, in the field of chemistry. In this list will be found such units, as: Foods, Beverages, Petroleum, Soaps, Organic Acids, Cosmetics, Alcohols, and approximately a dozen others selected and organized to afford maximum interest and utility in the solution of live needs, present and future.

Guiding the Pupils' First Steps in High-School Chemistry

CARROL C. HALL[1]
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HOW can the first class sessions with a beginning group in high-school chemistry be most profitably spent? This question must be answered. If not, the teacher's instruction is likely to be ineffective.

The first class sessions must be planned! They cannot be left to chance. Good guidance for the pupils' first steps aids greatly in the development of desirable learning habits and attitudes.

Before any suitable learning activities can be planned for the beginning classes a set of learning objectives must be drawn up for this phase of the instructional procedure. Here are some suggested objectives:

(1) To acquaint the pupils with the instructor and the instructor with the pupils
(2) To establish the mechanics of laboratory and classroom administration
(3) To review the objectives of the course of instruction
(4) To become familiar with the literature of chemistry
(5) To study the organization of the course of study
(6) To stimulate interest in chemistry
(7) To instruct in basic laboratory technics
(8) To teach certain fundamental skills essential for success in the study of any science

With the foregoing objectives in mind the teacher can now plan a series of classroom and laboratory activities which will have considerable influence on the pupils' future mastery of the subject matter.

Following are some activities that have been used with success in beginning chemistry classes:

Testing the ability to observe.—During the first part of the class session the pupils are instructed to observe a simple laboratory demonstration. A series of objective questions is then given, leading to a discussion on observing experiments and demonstrations. An exercise of this nature is given in detail in "Science and General Education" (*1*).

An informal reading and browsing session.—If the chemistry lecture room contains a library corner, a browsing period can be well spent. Opportunity should be given for looking through reference books, periodicals, pamphlets, and other supplementary literature. This period should be followed by a discussion of the materials available; also, how to use library facilities not in the classroom.

Reviewing basic laboratory technics.—The author for a number of years has devoted at least one class lecture to a demonstration of a number of these fundamental processes. (A card-file listing of them is helpful.) The pupils repeat the demonstration in the laboratory with their own desk equipment.

Laboratory safety instruction.—Safety instruction, including such items as the handling of glass, strong chemicals, flames, and simple first aid, may provide a separate class session or be combined with the session on laboratory fundamentals. A set of lantern slides has been developed on safety in the laboratory (*2*).

Metric system drills.—This work, standard practice for high-school chemistry teachers, should be used in both classroom and laboratory. The work in the classroom includes a review of the basic ideas of the system and memory drill; laboratory work should include gravimetric and volumetric measurements.

A pupil-rating testing program.—Time spent in measuring pupils' abilities in fundamental science thinking is not wasted. Such a testing program will provide the instructor with a more adequate concept of the potential success of any particular pupil or class group. These tests afford material for class discussions. A few titles of such tests are listed:

A Test in the Elements of Problem Solving and Scientific Procedures (*3*)
A Scale for the Measurement of the Scientific Attitude (*4*)
A Test for the Measurement of Superstitions and Misconceptions (*5*)
A Test in the Elements of Scientific Thinking (*6*)
A Test Measuring the Ability in Learning Procedures in Science (*7*)

A student self-evaluation exercise.—By class discussion, informal written statements, or by checking a prepared form the pupils can evaluate their use of time, their interests, and other factors that may influence their success in the study of chemistry.

A laboratory inspection trip.—The writer has found it a good practice to take the new chemistry groups through the laboratory prior to their work in it. This is particularly valuable for girls, who are likely to be unfamiliar with a laboratory. This trip includes a survey of the general organization, an inspection of the stock room, an explanation of fume-hood operation, room cleanliness and safety regulations, fire extinguisher and fire blanket locations, and, finally, the location and contents of the first aid cabinet.

Laboratory locker inspection and equipment identification.—This may or may not be in conjunction with the laboratory inspection trip. It is best done as part of the program for the first regular laboratory session. There are printed tests available which may be used to check on student mastery of apparatus nomenclature.

Inspection of textual materials.—A considerable portion of one class session can be well spent in examining the organization and content of the basal text materials. As elementary as this may sound, many youngsters, unfamiliar with the glossary, index, and appendix ma-

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terials, use their texts only as directed during the course. Two excellent testing instruments have been developed to aid in this type of instruction. They relate to the use and location of reference information both in the textbook and from other sources (*8*, *9*).

Visual aids as introductory materials.—If the chemistry teacher is supplied with moving picture films, film strips, or slides, these may be used in the introductory sessions, accompanied by a class lecture. Considerable editing must be done in order to fit the visual materials for introductory work, as they are usually designed for the formal divisions of the course of study.

By means of a well-planned introductory period the beginning group in chemistry gradually assumes a desirable class attitude that will go far in making the year's work an interesting and profitable excursion. It must be kept in mind that such a program can become functional only when it is based on definite and well-grounded objectives and accompanied by appropriate and worth-while learning exercises.

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A Crystal Grows Up

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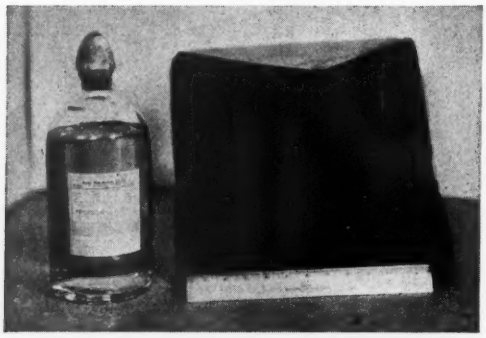
IN THE August, 1932, issue of the JOURNAL OF CHEMICAL EDUCATION there appeared my brief article describing means of preparing and preserving large crystals of chrome alum. Members of our school chemistry club have taken a considerable interest in crystal growing and have prepared fairly large crystals of many common laboratory salts such as the aluminum alums,



A CRYSTAL OF CHROME ALUM

Rochelle salts, copper sulfate, nickel sulfate, potassium ferricyanide, potassium ferrocyanide, etc., many of which were of interest because of the unusual crystalline forms exhibited. The pupils in elementary chemistry also show an intense interest in our brief discussion of crystals. Such being the case, we decided to allow the large crystal, described in the article previously mentioned, to grow as large as it would.

The crystal grew for nine and one-half years. Lack of constant temperature facilities caused many setbacks during the warm summers when, owing to the increased solubility of the alum, large fractions of the crystal redissolved, to be redeposited, only too often, on the bottom of the container. Obtaining large enough containers was another problem. After graduating from large beakers to laboratory crocks all went well until the average laboratory crock was too small. About this time we were fortunate enough to find the last container, a large glazed crock eighteen inches in diameter and having a capacity of about twenty-five gallons.

The crystal weighed, at the end of the year 1938, eighty pounds, or 36,287 grams, and was in excellent condition. Each edge of the triangular faces measured fourteen inches, or 35.5 centimeters in length. The photograph shows its size then in relation to the standard two and one-half-liter bottles found in every laboratory, and to a one-foot ruler.

The crystal was removed from the saturated solution in May, 1939, preparatory to being exhibited at the World's Fair in Flushing. At that time it weighed ninety pounds. It was given a protective coat of varnish to prevent efflorescence while out of the solution. The crystal was placed on exhibition in the Westinghouse Building as part of the science exhibit of the High-School division of the New York City School System where undoubtedly many readers saw it.

LETTERS

The Dimensional Method of Problem Solving

To the Editor:

In his paper on "The Solution of Elementary Chemical Problems" in the August, 1940, number of the JOURNAL OF CHEMICAL EDUCATION, Spicer makes two suggestions: (1) that the student justify in writing each step of the solution, and (2) that "proportions" be discarded. These suggestions should meet with universal approval. They can be put into effect most simply and expeditiously by labeling with its proper dimensions each number involved in the solution.

In problems based on equations, such as Spicer suggests, the use of the proportionality constant, which is only one step away from the anathematized proportion, is unnecessary and can very profitably be replaced by a single dimensional setup:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

$$\text{wt. } H_2 = 10 \text{ g. Zn} \times \frac{1}{65.4 \frac{\text{g. Zn}}{\text{mol Zn}}} \times 1 \frac{\text{mol } H_2}{\text{mol Zn}} \times 2 \frac{\text{g. } H_2}{\text{mol } H_2} =$$

$$\frac{10 \times 2}{65.4} = 0.31 \text{ g. } H_2$$

Of course both this method and Spicer's are only proportions in disguise, but the dimensional method is two steps away from the straightforward proportion.

By the dimensional method the cited gas-laws problem becomes:

$$\text{volume} = 6 \text{ l.} \times \frac{\text{pressure}}{\text{pressure}}$$

and, since the pressure is *decreasing* from 700 mm. to 500 mm., we must get for the answer a volume *greater* than 6 liters. Hence the larger pressure must be in the numerator and

$$\text{volume} = 6 \text{ l.} \times \frac{700 \text{ mm.}}{500 \text{ mm.}} = 8.4 \text{ l.}$$

To find the molar concentration of a solution containing four grams of NaOH in 300 cc. of solution, we proceed as follows:

The concentration in mol/l.

$$= 4 \text{ g. NaOH} \times \frac{1}{40 \frac{\text{g. NaOH}}{\text{mol NaOH}}} \times \frac{1}{300 \text{ cc.}} \times 1000 \text{ cc./l.}$$

$$= 1/3 \text{ mol/l. or } 1/3 \textit{ M}.$$

Finally, to find the freezing-point lowering of a solution containing three grams of methyl alcohol in 100 grams of water, we use the dimensional method:

$$\text{lowering} = \frac{3 \text{ g. } CH_3OH}{32 \frac{\text{g. } CH_3OH}{\text{mol } CH_3OH}} \times \frac{1}{100 \text{ g. } H_2O} \times 1000 \text{ g./kg.} \times$$

$$1.860 \frac{\text{deg.}}{\frac{\text{mol } CH_3OH}{\text{kg. } H_2O}} = 1.74°$$

These solutions are just as logical and expressive of the student's grasp of the problem, and are far shorter than the solutions given by Spicer. They have also the advantage that the complete numerical solution is set up before any calculations are performed so that any short cuts by cancellation are quite obvious.

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Atomic Weight Unit

To the Editor:

In the November, 1940, JOURNAL, Mr. Fred Fordemwalt asks, "Why hasn't this unit ever been given a name?" He is referring to an atomic weight unit.

It has, the microcrith. This is defined in the Unabridged Standard Dictionary as "the weight of the hydrogen atom." It is also defined in Williams' "Introduction to Chemical Science" (1888), my first chemistry textbook. Both Williams and Newth (1907) use the term crith for the weight of one liter of hydrogen. I have not seen these terms in recent texts. At that time hydrogen was the standard, with the atomic weight of oxygen 15.96. I also noted with interest that the number of molecules in a liter was given as 10^{24} in 1888.

Crith is from the Greek word for barleycorn and was used to indicate a very small weight.

I believe with Ostwald that the atomic weight is "a definite number which either by itself, or when multiplied by a whole number, determines the quantity that enters into compounds." Atomic weights are *ratio numbers*. There must be a standard, (as O equals 16) but do ratios have units?

S. FRANCIS HOWARD

NORWICH UNIVERSITY
NORTHFIELD, VERMONT

To the Editor:

Fred Fordemwalt brings out a very difficult point in the teaching of general chemistry: what is the unit for our atomic weights?. . . It seems to me that the use of such a word as "pel" would lead immediately to the difficulty of defining it. If the students did not ask for a definition of the word they would surely inquire concerning its origin. . . .

WILLIAM C. FRISHE

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Editor's note: Mark us down among the inquisitive, too. And we wonder whether the "pel" is a small enough unit, for its diminutive would seem to be "pellet," which we recollect as a rather large chunk of stuff.

Encyclopedia of Chemical Reactions

To the Editor:

The Encyclopedia of Chemical Reactions, first proposed in 1933 [See J. CHEM. EDUC., **10,** 614 (1933)] is now on the road to publication. When it finally reaches the publication stage, much credit must be given to the editors of this JOURNAL. Dr. Reinmuth accepted for publication my first article on the E. C. R., and as a result of this I was brought in contact with nearly a dozen chemists who have either assisted with the abstracting of chemical reactions or given me material aid and encouragement for the project.

I also wish to acknowledge my indebtedness to the present editorial staff for publishing my letter in the September, 1940, number of the JOURNAL, which was instrumental in finding a publisher for the E. C. R. as well as another abstractor.

The work has now taken on new life. The Chemical Publishing Company, Inc., of New York City, has agreed to publish the Encyclopedia of Chemical Reactions, and authorizes me to say that anyone wishing to join our list of abstractors, will, for a small contribution of his time, receive permanent recognition on the Board of Editors, besides the satisfaction of having helped in compiling a much needed work. One of the abstractors calls it "an indispensable reference work."

Abstracting assignments are still available for most of the German, French, and Japanese journals, and some of the English. Most of the American journals have been covered.

Any chemist wishing to become represented on the editorial board of this Encyclopedia should communicate with me, the temporary editor-in-chief.

C. A. JACOBSON

WEST VIRGINIA UNIVERSITY
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Symbols or Abbreviations?

To the Editor:

Many science teachers are annoyed, and students are often confused, by the great difference in usage with regard to the shortened designations for many of the common units which are such an essential part of scientific thinking. Herewith are a few examples taken from current scientific journals or texts:

For centimeter(s): cm., cm, cms., Cm., Cms.

For cubic centimeter(s): cc., c.c., cm^3, $cm.^3$, c cm., c.cm.

For gram(s): g., gm., gms., g, gs.

Would it not be apropos for the JOURNAL OF CHEMICAL EDUCATION to conduct a campaign among science teachers to point out that much of the confusion in connection with the shortened forms in referring to the fundamental units would disappear if scientists as a group would come to appreciate to a greater extent two facts: (1) that the various designations for the units are *symbols*, not *abbreviations;* and that (2) teachers should consistently use the *symbols* as recommended by some body or organization whose standing as a scientific body is unquestioned. In this country, this would logically be the National Bureau of Standards.

As custodian of the customary English and metric systems of measurements in the United States, the National Bureau of Standards has made specific recommendations as to the spelling and symbols of all the commonly used units. Scientific workers as a class might well familiarize themselves with the principles back of the recommendations of the Bureau of Standards:

(1) The period is not used in the shortened designation for a unit, thus making it a symbol, not an abbreviation. The only common exception to this rule is where the shortened form is an English word. For example, to avoid possible confusion with the word ***in***, the designation ***in.*** is used for the word ***inch.***

(2) The exponents "2" and "3" are used to signify "square" and "cubic" instead of the abbreviations "sq." and "cu." This does away with the designation *cc.* for cm^3 and *sq. cm.* for cm^2.

(3) The same symbol is used "for both singular and plural."

(4) Small letters are used for all shortened designations, except in the case of A for Angström.

These principles conform to the recommendations of the International Committee on Weights and Measures.[1]

As illustrative of the application of these principles, the following examples can be cited:

Unit	*Symbol*	*Unit*	*Symbol*
centimeter	cm	milliliter	ml
cubic centimeter	cm^3	inch	in.
decimeter	dm	micron	μ
foot	ft	millimicron	$m\mu$
kilogram	kg	milligram	mg
millimeter	mm	pound	lb
gram	g	square centimeter	cm^2

Strictly speaking, the cubic centimeter and milliliter are not identical because the liter is not exactly a cubic decimeter. "The liter is a secondary or derived unit of capacity equal to the volume occupied by the mass of one kilogram of pure water at 4°C." Actually, one liter is equal to 1.000027 cubic decimeters. Hence, the milliliter is larger than the cubic centimeter by 0.000027 cm^3. While for all practical purposes this is a negligibly small quantity, nevertheless all volumetric glassware is graduated in liters and milliliters, and chemists as a group should recognize that the designation *milliliter* is preferable to *cubic centimeter* as a unit of capacity.

C. E. RONNEBERG

HERZL CITY JUNIOR COLLEGE
CHICAGO, ILLINOIS

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[1] "Proces-verbaux des séances de 1879," Comité International des Poids et Mesures, 1880, Vol. IV, p. 41.

What's Been Going On

Starch Chemistry

STARCH is now being acetylated to give three types of products: (1) those soluble in water, (2) those soluble in both water and organic solvents, and (3) those that are soluble only in certain types of organic solvents.

Sweetose is obtained from corn starch by a combined acid-enzyme hydrolysis. It is sweeter and less viscous than ordinary corn sirup, is permanently clear, and does not crystallize on standing. It is normally marketed, slightly flavored, as Staley's Waffle Syrup.

Acid hydrolysis of starch, in the presence of molybdenum salts, gives a sirup with a high dextrose content and a desirable degree of fluidity. It is known as liquid sugar, and will find use in the confectionery trades.

Fro-Dex, Dri-Dex, and Malto-Dextrine are among the newer crystalline sugars. They are produced by the vacuum pan drying of appropriate corn sirups.

Levulinic acid, which is 4-ketopentanoic acid, is being produced from waste sugars and starch by a special acid hydrolysis. This makes another addition to the long list of carbohydrate products that are now commercially available.

The depolymerization of starch may be effected by (1) the wet process, or (2) the dry process. In the former, the nature of the end product is determined primarily by the hydrogen-ion concentration and the time of heating, whereas in the latter there are four variables: the moisture content of the starch, the concentration of the hydrogen chloride, the temperature of the reaction, and the time of heating. The use of these processes, together with different types of starch as starting materials, give rise to a large number of products with distinctly different physical properties.

According to G. E. Hilbert, Chief of the Starch and Dextrose Division at the Northern Regional Laboratory, about 80,000,000 pounds of starch were used last year in place of sodium silicate in the manufacture of corrugated cardboard by torrefying the starch *in situ*.

Increasing amounts of starch are being used in the sizing of painted walls. This enables the walls to be cleaned and resized when needed by washing with a starch solution.

The production of a starch engine, which will operate on pulverized starch, seems a little distant but no more so than did the airplane a few years ago.

When ethylene chlorohydrin is used as a dedormitizing agent for potato tubers and gladiolus corms, it is converted, according to recent studies by Denny and Miller of Boyce Thompson Institute, to the gentiobioside. The gentiobiose, incidentally, is also foreign to these plants or exists in very small concentrations. This seems to be the first experimental evidence that glycoside formation is a part of a protective detoxication process.

Dormitization of potato tubers and gladiolus corms may be effected, according to Denny and Guthrie of Boyce Thompson Institute, by treatment with a solution of potassium naphthaleneacetate or the vapors of methyl naphthaleneacetate. These dormitized tubers and corms may be dedormitized successfully by treatment with ethylene chlorohydrin. This suggests that dormitization may play an important role in the storage of various perishable farm products.

Fractional sedimentation of starch, over a period of about six weeks, gives two distinct fractions, one of which (the more soluble) seems to be of the long chain variety whereas the other (the less soluble) has a tree-like structure.

The use of the dropping mercury cathode, the formation and subsequent decomposition and analysis of thioacetals, and fractionation of alkylated derivatives are the newer methods that are being applied to a study of the progressive degradation of the starch molecule.

—ED. F. DEGERING

Liquid Oxygen Explosives[1]

LIQUID oxygen explosives as formerly made from a carbonaceous absorbent and relatively pure liquid oxygen presented serious hazards owing to their high inflammability. These mixtures are high explosives of good strength, which are useful for certain operations in the open, such as the strip mining of coal or open-cut metal mining. Because of their potential capacity for producing large quantities of carbon monoxide, their use underground or in confined places cannot be recommended. Because of the spontaneous evaporation of liquid oxygen under ordinary atmospheric conditions, these explosives have a short life; this gives rise both to unique safety features and to limitations in their application.

A recent coöperative investigation at the Bureau of Mines[2] has developed procedures for treating a granular carbonaceous absorbent and a canvas wrapper used commercially in liquid oxygen explosives to render these markedly fire-resistant. Phosphoric acid proved the most effective material of those examined for application to the granular carbonaceous absorbent; and aqueous solutions of mono- and di-ammonium phosphates, ammonium chlorides, and phosphoric acid gave very good results in applications to the canvas wrapper for cartridges. These fire-retardant treatments render the explosive immune to practical sources of ignition without serious detriment to its useful physical and explosive characteristics, and substantially eliminate the possibility that accidental ignition may develop into dangerous detonation.

—A. R. T. DENUES[3]

FROM the General Electric Research Laboratory comes the announcement of an electron accelerator, operating on an induction principle. It is a glass doughnut of less than a foot in diameter, looks somewhat like a miniature cyclotron, but is capable of handling electrons instead of positive ions. The accelerator's magnet, composed of thousands of small pieces of iron, can be used on alternating current. Instead of encircling the magnetic core by following a coil of wire, as they do in a power transformer, electrons in the induction accelerator are free to circulate about the magnetic core in the doughnut-shaped vacuum tube. Hence they make many revolutions, in 200,000 of which they travel 60 miles and gain 2,300,000 volts energy. When directed against a target the electrons from the present laboratory model produce radiation equivalent to that of 10 millicuries of radium.

PROFESSOR N. Henry Black, author of popular chemistry and physics textbooks, has retired from active teaching at Harvard University. On November 22, 1940, a group of his friends and colleagues gathered at the Harvard Faculty Club in Cambridge, Massachusetts, to honor him. Responses were made in behalf of several large groups of teachers. In conclusion Dr. Black related a few anecdotes from his experiences, including the story of a formal dinner with Sir J. J. Thomson.

TERGITOL T, a reagent to decrease surface tension, is found to be useful for assisting the separation of the precipitate when the centrifuge is employed. It is also a valuable aid in stabilizing colloids such as silver chloride for nephelometric measurements.

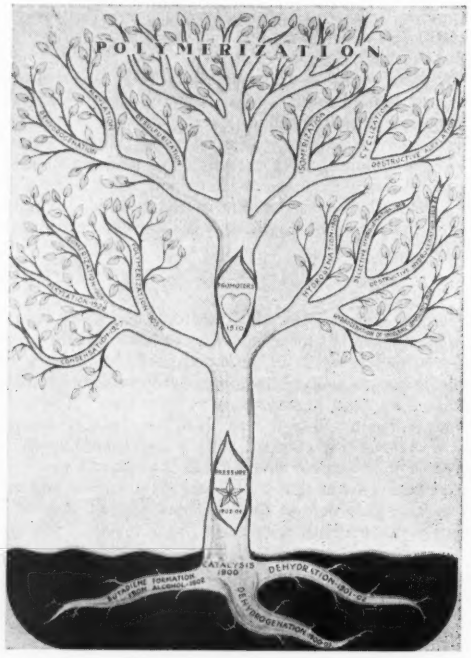
[1] Contribution from the Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania. Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not subject to copyright.

[2] A detailed account of this coöperative work may be found in Bureau of Mines Bulletin 429.

[3] Assistant chemical engineer, Explosives Division, Central Experiment Station, Pittsburgh, Pennsylvania.

Out of the Editor's Basket

ALLEN Scattergood, of Union Junior College, Roselle, New Jersey, makes a suggestion concerning the exercise in fractional distillation, generally included in the organic laboratory course. By using isomeric substances instead of the usual alcohol–water, or toluene–CCl_4 mixtures, students are given an opportunity to study the properties of isomers as well as to make fractional separations. He uses the normal and tertiary butyl alcohols, the latter of which may be obtained from the Standard Oil Company, Bayway, New Jersey. The separation is so efficient that care must be taken to avoid freezing of the tertiary alcohol in the condenser.



IPATIEFF'S CATALYTIC TREE

● On a recent occasion Dr. Vladimir N. Ipatieff, well-known contributor to petroleum research, made some observations pertinent to chemical education which we would like to quote directly:

"Most theoretical chemical investigations carried out in the silence of scientific laboratories, sometimes with a purely scientific purpose, sooner or later are utilized by the industry and thus serve humanity; such is the lesson that history teaches us. However, these discoveries must also serve the science by facilitating the study of it and its methods in universities and technical schools. The development of catalysis during the last thirty-five years has made it much easier to obtain many classes of organic compounds, and catalytic methods have replaced the older methods used in the laboratory. The reactions, which formerly required a period which ran into days and sometimes months, can now be carried out with the aid of catalysis within a few hours. The time has come when serious attention should be paid to the teaching of organic and inorganic chemistry—replacing the out-of-date reactions by new catalytic ones and trying to acquaint the students with the general phenomena of catalysis along with the more accepted hypotheses.

"To determine the structure and functions of the different classes of chemical compounds we must keep only those of the older reactions which are absolutely necessary for that purpose. When it comes to methods of synthesis of compounds new catalytic reactions should be introduced. There is no need to crowd the textbooks, especially in organic chemistry, with reactions which no one ever uses at the present time and which are absolutely unessential to the understanding of the fundamentals of a scientific subject.

"My opinion is that this will make it easier to master the courses in chemistry and the younger generation will be introduced to new ideas and will thus develop the *field of catalysis* for the chemistry of the future."

The fact that Dr. Ipatieff has himself contributed so much to our knowledge of catalysis makes these remarks especially appropriate. We also reproduce here his Catalytic Tree, showing the history of the application of catalytic processes to petroleum technology. The dates refer principally to his own researches in these particular branches (and roots) and give some idea of the debt which the petroleum industry owes to him.

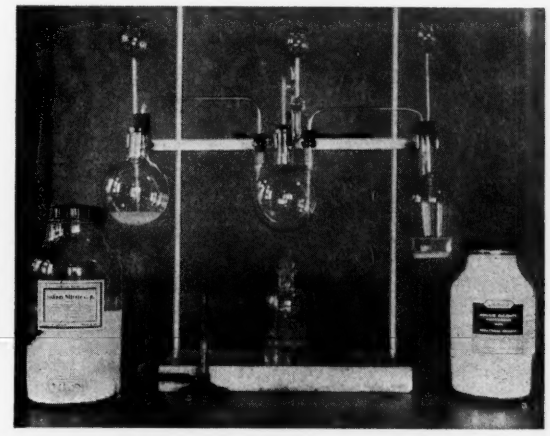
● Leonard F. Ford, of State Teachers College, Mankato, Minnesota, contributes two interesting demonstration experiments: (1) Moisten the wick of a candle with a saturated solution of white phosphorus dissolved in carbon disulfide, taking care not to spill any on hands or clothes; (2) add a few drops of water to a large ball of excelsior containing a little sodium peroxide. Either experiment produces results in a few moments! And perhaps you know this one: Paint a card with stripes of potassium thiocyanate, silver nitrate, and potassium ferrocyanide; upon sponging with a solution of ferric chloride a red, white, and blue flag will appear.

● The General Electric Laboratories have reported a newly discovered use of columbium, a relatively unfamiliar element with little commercial importance at present. It produces an alloy of unusual properties when added in small amount to iron. Samples containing three per cent of columbium in iron show exceptionally good rupture strength at 1100°F., a temperature not yet commercially used but being approached by modern high-temperature, high-pressure steam turbines. No carbon is contained in the alloy, so it is not a steel; instead, the columbium is present as a finely dispersed stable compound of iron and columbium.

● R. D. Billinger, of Lehigh University, got to wondering about college laboratory manuals in elementary chemistry—those published in the last ten years—and

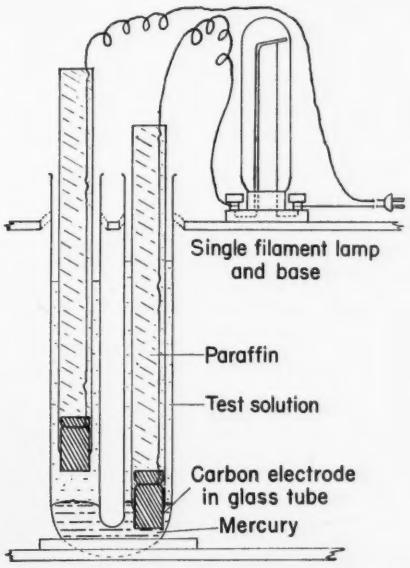
he looked through them to find the amount of emphasis placed upon quantitative experiments. He found that although the percentage of these varied between five and sixty-two per cent, in most of them from twenty to thirty-five per cent of the experiments were quantitative in nature. The tendency seems to be an increase in this direction and toward experiments which illustrate general principles. We are gratified to note that he reports the frequent inclusion of experiments developed in this JOURNAL.

● Showell C. Dennis, of Girard College, sends in the accompanying illustration of a setup to demonstrate the chamber process for H_2SO_4. The Wulff flask in the center is the reaction chamber and carries a double-bend safety tube containing water. Nitric acid is generated in the left-hand flask by sulfuric acid and sodium nitrate; sulfur dioxide in the right-hand flask by sulfuric acid and sodium sulfite. By filling the reaction chamber with nitric acid fumes and then running in SO_2 the "chamber crystals" of nitrosyl sulfuric acid can be formed, and on addition of water H_2SO_4 results.



CHAMBER PROCESS FOR SULFURIC ACID

● Jack De Ment, of Portland, Oregon, tells how polaroid may be used to distinguish between true fluorescence and diffusion of light, in minerals and other substances. When a fluorescing specimen is examined with polaroid the density of light is reduced simply in proportion to the absorption of the polaroid; but when the specimen diffuses light a partial extinction will result, since a fraction of the diffused light will be polarized.



CONDUCTIVITY OF SOLUTIONS APPARATUS

● Another one of the many types of "conductivity apparatus" has been contributed by W. T. Wilks, of Tallahassee, Alabama. The illustration will show its use. The carbon electrodes, embedded in paraffin in large glass tubes, are obtained from flashlight batteries. By alternately raising the electrodes to the same height above the mercury in the bottom of the U-tube the relative conductivities of two test solutions may be compared by the brightness of the lamp. The effect of mixing two solutions may be shown by tilting the U-tube several times.

RECENT BOOKS

CHEMISTRY. *G. Oppe*, Head of the Science Department, Ball High School. The Steck Company, Austin, Texas. 160 pp. 66 figs. 20.5 × 26.8 cm. $0.36.

This "workbook" for high-school use seems to stand out from among the increasing number of similar publications. The illustration on its cover—A New World—shows a fascinated youngster experimenting in his basement laboratory and is the "theme song" of the book. The first paragraph of the introduction supplies the words:

"'A new world'—that is what a study of chemistry is going to help you discover. Your world is different from that of your grandfather's because nearly everything you use has been created or improved by chemical research."

A large element in the attractiveness of the book is the well-chosen selection of halftone illustrations.

N. W. RAKESTRAW

BROWN UNIVERSITY
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STATISTICAL MECHANICS. *J. E. Mayer* and *M. G. Mayer*, Columbia University. First Edition. John Wiley and Sons, Inc., New York City, 1940. xi + 495 pp. 28 figs. 15 × 23 cm. $5.50.

The first chapter of this book gives a simple and well-written account of the elementary properties of an ideal gas and serves to illustrate the statistical method. Some of the subjects dealt with are the Maxwell-Boltzman distribution law, mean free path, viscosity, heat conduction, and diffusion.

A summary of important equations of classical and quantum mechanics together with a discussion of the fundamental hypothesis of statistical mechanics is given in chapter two. This is followed by a development, in the next two chapters, of fundamental statistical equations and the laws of thermodynamics.

The early introduction of the languages of quantum mechanics and of thermodynamics is an outstanding feature of this book, as it enables the authors to express the necessarily abstract laws of statistics in familiar terms.

The remaining portion of the book deals with the practical applications of the subject. The topics discussed are: the thermodynamic properties of monatomic and polyatomic ideal gases including chemical equilibrium; elementary properties of ideal crystals; non-ideal gases and phase integrals; electric and magnetic fields; and, in the last chapter, the applications of Bose-Einstein and Fermi-Dirac statistics to the problems of black body radiation, elementary properties of metals, and degenerate gases. The appendix contains an excellent collection of useful mathematical formulas, numerical tables and physical constants.

The book represents an ideal compromise between a massive treatise and a condensed summary. Many of the topics could be discussed further in great detail. However, the material selected serves well to illustrate the methods of statistical mechanics and all of it is of practical importance to a physical chemist. The reviewer feels that many discussions could be made clearer by giving a direct comparison between theoretical and experimental results; very few experimental data are given.

JOHN R. LACHER

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THE MATHEMATICAL THEORY OF NON-UNIFORM GASES. *S. Chapman*, M.A., D.Sc., F.R.S., Professor of Mathematics, Imperial College of Science and Technology, London, and *T. G. Cowling*, M.A., D.Phil., Lecturer in Mathematics, the University, Manchester. Cambridge University Press, 1939. xxiii + 404 pp. 13 figs. 17 × 26 cm. $7.50.

While the book under review seems to make only a limited contact with chemistry, there are important chemical potentialities in the subject it covers. For example, the most recent method for the separation of isotopes depends on a phenomenon discovered theoretically by Chapman.

This book is in no sense a textbook, although a fairly extensive mathematical introduction is included. It will undoubtedly remain for many years the standard reference for the mathematical treatment of transport problems in the kinetic theory of gases.

E. J. ROSENBAUM

THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

THE MICROSCOPE. *R. M. Allen*. D. Van Nostrand Company, New York City, 1940. viii + 286 pp. 82 figs. 15 × 23 cm. $3.00.

This volume is written for the layman and for those individuals with no training in even the most basic principles of physics and optics. It is, therefore, very elementary.

This work will find its way into the hands of amateur microscopists, and it will have a useful place on the reference shelf of high-school laboratories and science clubs. It was not written for, nor will it satisfy, professional workers.

F. J. PETTIJOHN

THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

CHEMICAL COMPUTATIONS AND ERRORS. *Thomas B. Crumpler*, Ph.D., Assistant Professor of Chemistry, The Tulane University of Louisiana, and *John H. Yoe*, Ph.D., Professor of Chemistry, University of Virginia. First Edition. John Wiley and Sons, Inc., New York City, 1940. xiv + 247 pp. 16 figs. 15 × 23 cm. $3.00.

This book is planned to fill a number of gaps in the mathematical education of most chemists. It is true that the elementary material on exponents, logarithms, and the slide rule is ordinarily acquired fairly early in the training of a chemist, but this discussion is so well done that it might properly serve as a model for teachers of chemistry who find it necessary to give that computational skill to their students. The chapter on significant figures, however, contains nothing which might not be found in any textbook of quantitative analysis. The chapters on solving equations, and especially the material on interpolation and extrapolation, are important and not particularly easy to find elsewhere. The presentation of the theory of measurement goes considerably beyond the common works on quantitative analysis, and the chapter on the classification of errors employs examples selected from many sources, evidently in order to teach the habit of searching for errors in all sorts of experiments.

Some seventy-five pages are devoted to a very detailed and well-studied presentation of the statistical theory of random errors and its practical application to problems of measurement.

The final chapter describes the art of "curve-fitting," by which one may find an equation approximately describing a set of empirical results. The method of least squares is shown to be an effective way of finding the most appropriate parameters. This material is a definite requirement for a great deal of the research work now carried on in physical chemistry.

Each chapter is followed by many illustrative problems (with answers at the end of the book), and these add greatly to the value of the work.

ANTON B. BURG

UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA

FARMWARD MARCH. *William J. Hale*, Ph.D., L.L.D. Coward-McCann, Inc., New York City, 1939. xi + 222 pp. 12.5 × 18.5 cm. $2.00.

Written in popular style, the book is aimed to create and stimulate interest in the important field of farm chemurgy. However, in view of the many fantastic statements and predictions, it may be that the author has defeated his own purpose. From the standpoint of a sound discussion of the possibilities of farm chemurgy there is little basis for commendation of the book.

H. R. KRAYBILL

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

VITAMIN E. A Symposium, Society of Chemical Industry. Edited by *A. L. Bacharach* and *J. C. Drummond*. Chemical Publishing Co., Inc., New York City, 1940. viii + 88 pp. 2 figs. 15 × 22 cm. $2.00.

The book is divided into three parts: (1) the chemical structure and properties of tocopherol (vitamin E); (2) the physiological action of vitamin E and the consequences of vitamin E deficiency; (3) clinical and veterinary uses of wheat germ oil and vitamin E preparations. Each of the papers, presented at a symposium April 22, 1939, is documented by references to original papers, totaling 165; these are combined into a single alphabetical bibliography. There is no index.

Though the individual papers are brief, they were carefully prepared by an outstanding group of investigators. The editing and printing have been done carefully. Anyone interested in the theoretical or practical aspects of vitamin E will find the book a valuable reference. In a field of study that is moving rapidly and characterized by many differences in ideas, it is particularly valuable to have such an adequate cross-section of current opinion.

C. G. KING

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

TWELFTH REPORT OF THE COMMITTEE ON CATALYSIS. *National Research Council.* John Wiley and Sons, Inc., New York City, 1940. x + 338 pp. 6 figs. 15 × 23 cm. $5.00.

"The intention of this report is to present a somewhat critical and proportioned impression of the state of progress of catalysis, with a resumé of the important work published since the appearance of the eleventh National Research Council report." This volume covers the three-year period 1935–37. Equal emphasis is placed upon the importance of contributions from the industrial and the academic research laboratories.

The report is not encyclopedic; there are, however, over 1700 references to the journal and patent literature which are the more valuable because they comprise a selected list. The usefulness of the undertaking is enhanced by the inclusion of critical reviews of fifteen books on catalysis published during the three-year period under consideration.

In summarizing the present position regarding the current theories of catalysis the committee has been guided by the principle that "the phenomena of catalysis are probably too complex to fit a single mechanism," and hence tendencies to overemphasize one aspect of the subject are held in check. The reviewer is glad to find an authoritative and unbiased estimate of the validity of the concept of active centers as well as of the theory of activated adsorption. Although recent experimental evidence indicates that neither of these concepts is universally applicable in contact catalysis, the reviewer agrees that both are useful and apparently indispensable in the interpretation of a broad range of experimental results related to many types of catalytic action.

This volume will obviously be most helpful to the specialist in catalysis whether he be interested in the theoretical or the applied aspects of the subject, but no student of chemistry can fail to find many points of interest between its covers.

RALPH A. BEEBE

AMHERST COLLEGE
AMHERST, MASSACHUSETTS

CHEMICAL CALCULATIONS. *J. S. Long*, Chemical Director, Devoe & Raynolds Co., formerly Professor of Chemistry, Lehigh University, and *H. V. Anderson*, Associate Professor of Chemistry, Lehigh University. Fourth Edition. McGraw-Hill Book Co., Inc., New York City and London, 1940. x + 266 pp. 16 figs. 14.5 × 21 cm. $1.75.

This new edition is the work of the junior author, Professor H. V. Anderson. It differs from the previous edition (*cf.* J. CHEM. EDUC., **9**, 968 (May, 1932)) in that the descriptive part has been wholly rewritten. In the words of the author, "Certain rearrangements of the subject matter have been made, and additional material is included to bring the book within the scope of modern trends in scientific thought and practice." The most noteworthy change is the introduction of the new theory of atomic structure, so that oxidation-reduction equations can be presented from the electronic viewpoint. A few new problems have been added to the previous edition, bringing the total number up to eight hundred forty-five.

J. H. REEDY

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

ON OXIDATION, FERMENTATION, VITAMINS, HEALTH AND DISEASE. *Albert V. Szent-Györgyi*, M.D., Ph.D. (Cantab.), D.H.C., Prix Nobel, Professor of Medical and Organic Chemistry, University of Szeged. The Williams and Wilkins Co., Baltimore, Md., 1939. xi + 109 pp. 14 figs. 13 × 20.5 cm. $2.00.

The book contains the five lectures delivered by Dr. Szent-Györgyi in the Sixth Series of Abraham Flexner Lectures at Vanderbilt University. It represents a summary of Dr. Szent-Györgyi's research in the field of biological oxidation during the past fifteen years.

C. A. ELVEHJEM

UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

PROTECTIVE COATINGS FOR METALS. *R. M. Burns*, Assistant Chemical Director, Bell Telephone Laboratories, and *A. E. Schuh*, Director of Research, United States Pipe and Foundry Co. Reinhold Publishing Corp., New York City, 1939. vi + 395 pp. 89 figs. 15 × 23 cm. $6.50.

This monograph of the American Chemical Society Series of Scientific and Technologic Monographs is a successor to H. S. Rawdon's, PROTECTIVE METALLIC COATINGS, which appeared in 1927. In the important field of protective coatings for metals, research has been going forward in many laboratories, university, governmental, and industrial. The quantity of work that has been put forth in the field of corrosion since 1927 has been so large that the authors have had to rewrite the original work of Rawdon.

This volume is definitely intended for chemists, metallurgists, and materials and construction engineers who are faced with corrosion problems. The teacher of chemistry will find this volume very valuable because it translates into practice many of the general principles of chemistry that are discussed in the classroom. From the standpoint of a teacher of chemistry, however, it is unfortunate that the authors have adopted European conventions in dealing with the potentials of metals in the electromotive series. The authors are to be congratulated on their excellent survey of the whole field of protective coatings, non-metallic as well as metallic.

C. E. RONNEBERG

HERZL JUNIOR COLLEGE
CHICAGO, ILLINOIS

ELECTROCAPILLARITY: THE CHEMISTRY AND PHYSICS OF ELECTRODES AND OTHER CHARGED SURFACES. *J. A. V. Butler*, D.Sc., University of Edinburgh. Chemical Publishing Co., Inc., New York City, 1940. viii + 208 pp. 56 figs. and 1 plate. 14 × 21.5 cm. $5.00.

The contents and scope of this book are described better by the subtitle than by the main title, for many of the subjects discussed would not normally be included under the heading of "electrocapillarity." The purpose of the author has been to deal with "potential differences at electrified interfaces, the origin and nature of the effects that arise therefrom, and with electrode equilibria and kinetics." In the first three chapters of the book the question of the origin of the E.M.F. of the galvanic cell is considered, and the thermodynamics, mechanism, and energetics of reversible electrodes are examined; the applications of such electrodes are, however, not included as this subject is adequately dealt with in textbooks of electrochemistry and thermodynamics. Topics which are usually included in the term electrocapillarity are treated in the third and fourth chapters; these are electrocapillary curves, electrical double layers and electrokinetic phenomena. The three concluding chapters deal with the most familiar instances of irreversible electrode behavior, including overvoltage, concentration polarization, and electrolytic oxidation and reduction.

Apart from a short historical introduction, the work described is restricted almost entirely to researches carried out during the past fifteen years. The author tends to lay special emphasis on his own work, but he justifies this by the statement that his chief motive in writing this book has been to give a connected account of the work with which he has been associated, and to present the subject as it appears to him as a result of these studies. The material is presented in a clear and concise manner, and the inclusion of adequate references to the original literature obviates any impression of personal bias. On the whole, therefore, the book gives a satisfactory picture of our knowledge of electrocapillary and electrode phenomena as at about the middle of 1939. Since much of the material presented is to be found only in scientific journals, this book should provide teachers of physical chemistry with valuable supplementary reading matter in connection with both electrochemistry and the study of surface phenomena. The high price of the book, for its size, will unfortunately militate against its general use by students.

SAMUEL GLASSTONE

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

PHYSIOLOGICAL CHEMISTRY, A Text-Book for Students. *A. P. Mathews*, Ph.D., Andrew Carnegie Professor of Biochemistry, University of Cincinnati. Sixth Edition. The Williams and Wilkins Co., Baltimore, 1939. xvi + 1488 pp. 113 figs. 16 × 23 cm. $8.00.

The new edition of this well-known textbook is bigger than its predecessors, in spite of the omission of the directions for laboratory work. The larger type makes the pages more attractive, but some of the illustrations seem to have become darkened by age. The subject matter is that which is usually taught in first-year medical courses, with particular consideration of the mammalian body as a mechanism. The stimulating quality of the author's style has not been dulled by the passage of years.

The reviewer feels that a book of this size should be, in spite of its sub-title, a useful and authoritative work of reference as well as a text for beginners in the subject. Its value might have been increased by more thorough discussion of recent work, by a more systematic method of referring to the literature, and by the inclusion of an author index. However, the book will be adequate, if supplemented by good teaching, for its intended purpose.

DAVID I. HITCHCOCK

YALE UNIVERSITY SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT

SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS. *H. Middleton*, Lecturer in Organic Chemistry, Bradford Technical College. Longmans, Green and Co., New York City, 1939. viii + 279 pp. 14 × 22 cm. $2.50.

Detailed directions are given for the rapid identification of a considerable number of organic compounds of the more common types. As the author states in the preface, "particular attention has been paid to the requirements of pharmaceutical students, the schemes permitting of the rapid identification of the majority of the single organic compounds included in the British Pharmacopoeia." The book is in no sense a textbook of qualitative organic analysis, explanations of the methods used being omitted entirely, but as a laboratory manual of exercises for undergraduate students it can be recommended.

WELDON G. BROWN

THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

THE PHOTOGRAPHIC PROCESS. *Julian Ellis Mack*, Assistant Professor of Physics, University of Wisconsin, and *Miles J. Martin*, Professor of Physics, Milwaukee Extension Center, University of Wisconsin. McGraw-Hill Book Co., Inc., New York City, 1939. xvii + 586 pp. 19 × 25 cm., $5.00.

The book is written as a textbook for a course in photography. It contains a large amount of miscellaneous information including a more or less empirical treatment of the parts of optics necessary for photographers, a discussion of camera types, a little about the photograph emulsion and the latent image, development, printing, and color photography. Appendices are given which cover some of the mathematical functions and symbols, some chemistry, a formulary, and a manual of directions for various operations.

For the person who has had little or no physics many sections of this book would prove to be difficult reading. For a person who has had at least elementary optics and one year of college chemistry most of the sections would prove interesting and intelligible. Since the book covers a large range of subject matter, a great deal has to be skipped over in a hurried fashion. Naturally much of the material dealing with photography is empirical in character. The book is, therefore, of great value to persons who wish to find gathered in one place a lot of information relevant to the practical aspects of the subject.

The book is filled with good illustrations and diagrams and contains also many very fine photographs. As a text for a practical course in the subject the book would seem to have been very well written, and it could also be very interesting reading for the amateur photographer who has had some scientific training.

W. ALBERT NOYES, JR.

THE UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

INORGANIC CHEMISTRY. *F. A. Philbrick*, M.A., Rugby School. G. Bell and Sons, Ltd., London, 1939. viii + 396 pp. 181 figs. 13 × 19.5 cm. 6d. Accompanied by FACTUAL TESTS IN INORGANIC CHEMISTRY, 80 pp., 1d., and ANSWERS TO FACTUAL TESTS IN INORGANIC CHEMISTRY, 11 pp., 6d. net, both by the same author and publisher.

This series of publications is designed to aid students in preparation for examinations in the English system of higher education. The three books are planned for use together, one as a textbook, one for examination, and one as a means of evaluating the accuracy of the test answers.

The INORGANIC CHEMISTRY is "essentially a book to learn from rather than a reference book overburdened with facts"..... "This book is offered in the belief that a good understanding of the foundations of the subject can be imparted without giving the student more (detail) than he can carry in his head." The book seems to be prepared mainly for review purposes in preparation for certain examinations, corresponding to our college entrance examinations or to the entrance requirements in inorganic chemistry in our medical schools. It would perhaps be classed as intermediate between a high-school and a college text.

FACTUAL TESTS IN INORGANIC CHEMISTRY contains an extensive series of new-style questions covering most of the factual material set forth in the author's INORGANIC CHEMISTRY. These questions are almost all of the multiple choice type. The author recommends that they be used for frequent testing of progress and suggests numerous short tests which need occupy but a few minutes both for the preparation of the answers and for the grading of the papers.

In the ANSWERS TO THE FACTUAL TESTS IN INORGANIC CHEMISTRY there is a brief discussion of the object of factual tests, suggestions on how to use these tests and the answers, arranged and numbered to accord with the questions.

These books are admirably suited to give a good review or a rapid survey of the essential facts of modern inorganic chemistry. The descriptive matter is excellent and the viewpoint is modern. American students would find little difficulty because of the English background. To the reviewer the books seem to be too advanced for a high-school text and too brief for a fundamental course in college chemistry.

B. S. HOPKINS

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

QUANTITATIVE ANALYSIS. *H. S. Booth* and *V. R. Damerell*. McGraw-Hill Book Company, New York City, 1940. xi + 246 pp. 15 × 22 cm. $2.25.

The text has been built entirely around the laboratory experiments as the topic of greatest importance in quantitative analysis. There is no separate treatment of theory, but this has been introduced by the method of small doses into the laboratory directions wherever they apply directly. Problems have been omitted with the explicit understanding that a separate book on calculations should be used in conjunction with the present laboratory manual. Either gravimetric or volumetric analysis may be given first. This alternative is unusually well provided for in the treatment of the subject matter.

By all odds the strongest point in favor of this new text is the remarkable clarity of the laboratory directions. Even casual examination proves that every sentence has been subjected to rigorous examination and critical study of each word. The student in elementary analytical chemistry is continuously kept in mind. Quite rightly very little is taken for granted relative to the chemical knowledge based upon only a single year of preparation.

The authors are to be thanked for making available to a wider group the results of their own exhaustive experience. The text, which is a member of the International Chemical Series, is uniform in printing and binding with other members of the Series, and these features are entirely satisfactory.

G. L. CLARK

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

TWO IMPORTANT REVISIONS

ELEMENTARY QUALITATIVE ANALYSIS FOR COLLEGE STUDENTS

New Third Edition

By J. H. Reedy, University of Illinois. *International Chemical Series.* 159 pages, $5^1/_2 \times 8$. $1.50

In revising this well-known manual the author has sought to combine the advantages of the semimicro and the macro techniques and at the same time to avoid the limitations of each. Besides including the semimicro approach to qualitative analysis, the present edition contains several other procedures: the new procedure for the Tin Subgroup; the use of alcohol in sensitizing the separations and tests in the Alkali Group; and a more definite procedure for the detection of the anions.

Throughout it has been the author's purpose to build procedures based on chemical facts within the range of the student's training. To this end the newer organic reagents have been avoided, as the aim has been, not to set up certain mechanical procedures for identifying unknown materials, but to teach the reactions of inorganic chemistry.

EXPERIMENTS IN GENERAL CHEMISTRY

New Third Edition

By Hosmer W. Stone, Max S. Dunn, and James D. McCullough, University of California at Los Angeles. *International Chemical Series.* 285 pages, $8^1/_2 \times 11$. $1.60

In its present revision the effectiveness of this successful manual has been considerably strengthened by the elimination of certain assignments and the addition of others, together with a number of important changes designed to improve the experiments. New Problems have been added to many of the assignments to adapt the manual more closely to the needs of students taking chemistry with a more technical objective.

The data and the problem forms used in the calculation of results from the experimental data have in many cases been recast and clarified.

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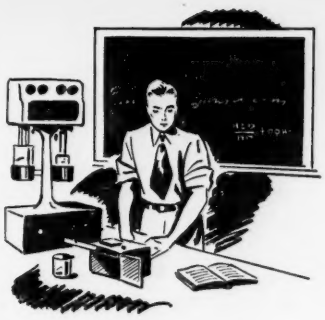

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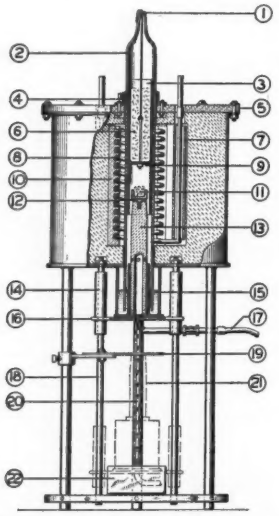
Sober Vertical Combustion Furnace

The accompanying diagram shows the details of the Sober Vertical Combustion Furnace, manufactured and sold by the *Hevi Duty Electric Company, Milwaukee, Wisconsin.*



1—Connected to Absorption Train. 2—Sillimanite Combustion Tube. 3—Adjustable Shield Protecting Combustion Tube from Spatter. 4—Holding Clamp for Combustion Tube. 5—Top Head, Asbestos (and Bottom). 6—Asbestos Fiber Insulation. 7—Terminal Insulators. 8—Alloy 10 Heating Coil. 9—Perforated Shelf. 10—Grooved Refractories Holding Coils. 11—Sample in Clay Crucible. 12—Nonoxidizing Metal Cap. 13—Pedestal of High Temperature Ceramic Refractory. 14—Elevator Slides. 15—Liquid Seal (Mercury). 16—Elevator Platform. 17—Oxygen Inlet. 18—Elevator Guides. 19—Adjustable Swinging Loading Shelf. 20—Counterweight Chain. 21—Loading Position of Pedestal. 22—Counterweight

It is claimed that this design makes possible the determination of carbon in materials by the direct combustion method—easy, rapid, and economical without sacrifice of accuracy.

Bulletin HD 1040, that can be obtained from the company, describes this furnace and those features claimed to be unique to it.

New "PYREX" Brand 6″ Desiccators

Corning Glass Works announces a new 6″ size "PYREX" brand Desiccator in two styles—No. 3118 with, and No. 3078 without sleeve, designed to make vacuum work easier and faster.

The new type valve supplied with No. 3118 desiccator embodies special features. The ⅎ 40/35 external sleeve acts as a stopcock. A one-quarter turn of the collar opens or closes the valve.

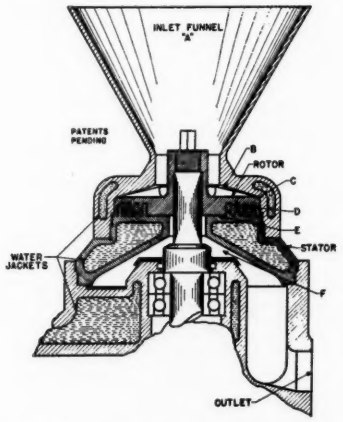
For greater convenience, an arrow, molded in the cap indicates open position. It is claimed that each desiccator passes a 24-hour test under vacuum and that a minimum mercury manometer reading of 20 inches, after the prescribed time limit, is provided for by manufacturing specifications. The special Corning method of grinding allows for the economical interchange of parts.

Pyrex brand Balanced Chemical Glass—balanced for mechanical strength, heat resistance, and chemical stability—is used in the construction of "Pyrex" desiccators, which are now available through laboratory supply dealers.

For further information write your dealer or *Corning Glass Works, Corning, N. Y.*

New Colloid Mill

The machine is of the vertical type. Material is fed downward through a receiving funnel "A" and encounters the impeller vanes "B" on top of the rotor traveling at 10,800 R.P.M., which force it to the periphery of the rotor at pressures as high as 150 pounds per square inch for some materials.



The material is sheared at "C" in passing downward between the side of the rotor and the housing (first processing action), is then impelled against centrifugal force by the pressure of oncoming material through a labyrinth of tight-fitting circular rings "D," machined on the bottom of the rotor and the top of the stator (second processing action), and then forced across the smooth section "E" between the rotor and the stator (third processing action) and drains from the chamber "F" through the side discharge outlet without having come in contact with any packing or glands at any time.

The labyrinth "D" is formed usually of plain rings machined on the bottom of the rotor and the top of the stator, but all or any of these rings may be cut clockwise or counter-clockwise with slots of various widths and spacings when additional cutting action is desired. Clearance between the stator and the rotor can be adjusted easily to meet the requirements of various materials, and the assembly then locked in the desired adjustment.

It is claimed that the machines can be dis-assembled and thoroughly cleaned in from two to three minutes. They are available in four sizes with 4″, 6″, 9″, and 12″ diameter rotors. Descriptive literature may be secured by writing to *The C. O. Bartlett & Snow Company, Cleveland, Ohio.*

Ohm's Law Calculator

An Ohm's Law Calculator, for which it is claimed that any Ohm's Law problem can be solved with one setting of the slide, is available from the Ohmite Manufacturing Company.

The calculator consists of sliding scales from which one can find the volts, amperes, watts, and resistance. One side of the card, which is 4″ × 9″, yields the above information for resistances up to one thousand ohms, and the other side has information for resistances between one thousand ohms and ten megohms. When the resistance is not known, the related values may be obtained by setting the scales on any two other values.

This sliding scale calculator may be obtained for ten cents by writing to the *Ohmite Manufacturing Company, Chicago, Illinois.*